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Gentlemen:-

In response to yours of the 1st we are  
very pleased to send you a copy of Phillips' FUNDA-  
MENTALS OF ORGANIC AND BIOLOGICAL CHEMISTRY.

Yours very truly,

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# FUNDAMENTALS OF ORGANIC AND BIOLOGICAL CHEMISTRY

BY

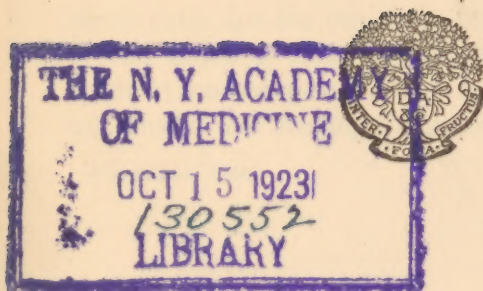
THOMAS GUTHRIE PHILLIPS, Ph.D.

PROFESSOR OF AGRICULTURAL CHEMISTRY  
IN THE OHIO STATE UNIVERSITY

WITH A FOREWORD BY

ALFRED VIVIAN

DEAN OF THE COLLEGE OF AGRICULTURE  
OF THE OHIO STATE UNIVERSITY



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MANUALS OF BIOLOGICAL  
AND MEDICAL CHEMISTRY

THOMAS GUTHRIE THOMPSON

ASSISTANT PROFESSOR OF PHYSIOLOGY  
IN THE MEDICAL SCHOOL

WITH A FOREWORD BY

ALFRED J. LEACH

ASSISTANT PROFESSOR OF PHYSIOLOGY  
IN THE MEDICAL SCHOOL

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## ACKNOWLEDGMENTS

In his foreword to this text, Dean Vivian has touched very lightly indeed on his own contribution to its development. Not only was most of the material selected and tested during his remarkably successful teaching of the subject, but also his interest has continued during the preparation of the text, and whatever is good in its content and arrangement is due largely to his valuable advice and constructive criticism.

Professor J. F. Lyman of this department, and Professor H. C. Sampson of the Department of Botany have helped greatly in the selection of material, particularly for the last three chapters.

The author is deeply indebted to his wife for her constant encouragement and help in preparing the manuscript and reading the proof.

COLUMBUS, OHIO





## FOREWORD

A century or two ago there was no particular difficulty in deciding what should be taught in a college curriculum. The number of subjects recognized as being worthy of study, and the amount of knowledge which was in teachable form were so small that the entire ground could be fairly well covered in the usual years of college residence. The past century, however, has seen the accumulation of vast stores of information, and the development of many lines of study that were unknown to earlier ages. Especially remarkable has been the growth of science during that period with its great additions to our fund of knowledge. It is undoubtedly true that the science of chemistry alone now has a greater content than had all the sciences put together a century ago, and the growth of the other sciences has been proportionately great. Along with this advance in our knowledge of science itself has come the rapid development of those vocations which are based on science, and the consequent introduction of specialized curricula into the colleges and universities.

It is now evidently impossible for any one person to master all the information in all of the sciences, and even within each science the advanced student finds it necessary to devote his major effort to a more

or less restricted area of the general field of that science. The different sciences are so closely interlocked, however, that the student of one science finds it necessary to have some knowledge of all the others. Some knowledge of chemistry, for instance, is needed by the students of any of the other sciences, and by those preparing for any of the vocations based upon the applications of science. Since only that student who is majoring in chemistry can undertake to master the large content of that science, it follows that the student of another science or vocation, who must devote most of his time to his major line, must either be denied the privilege of studying chemistry or be provided with a briefer course than that offered for the student majoring in the subject.

The short course in science has been in bad repute in the past largely because the method of shortening the course consisted in an attempt to cover the entire field of the science in a superficial way. Such a course often confused rather than enlightened the student, and left him with no workable knowledge of the subject. The better way to construct a brief course is to avoid trying to cover the entire field of the science and to select for presentation those fundamental facts and principles which will function in the life work of the student for whom the briefer course is arranged. Such a course, if properly constructed, is not superficial, since each fact and principle is thoroughly presented. It does save time for the student by eliminating most of the material which does not function in his line of major endeavor, which, after all,

is a good educational principle to observe in arranging any course or curriculum. One of the functions of a teacher should be to sift the material at his disposal and to make a wise choice as to what part of his knowledge is worth presenting to the particular student group that is under his instruction.

In this text, Dr. Phillips has followed the method of preparing a brief course in the fundamentals of organic and biological chemistry by carefully selecting that material which is of importance to the student who is not majoring in chemistry, but who needs some knowledge of chemistry to enable him to understand certain other facts and principles which are fundamental to his major science or to his chosen vocation. In this small book will be found those facts and principles of organic and biological chemistry that should be known by all students of those sciences which deal with plant or animal life. The course as presented is intended to follow the usual collegiate course in elementary chemistry, and, brief as it is, contains as much of organic and biological chemistry as the ordinary student, who is not primarily interested in chemistry, is likely to need. With slight additions (as, for instance, from the cyclic compounds) it will fill the requirements of many other groups than those for which it was originally intended, and thus serve the needs of many groups with limited time to devote to chemistry.

This text does not represent an untried experiment. For at least fourteen years practically the course outlined in this text has been taught at the Ohio State



University, the teaching for the first part of that time being in the hands of the writer of this foreword. Dr. Phillips in his six or seven years of experience with the course brought the material together, arranged it in order for presentation, and thoroughly tried it out with the help of a mimeographed text placed in the hands of his students. It is, therefore, presented to the public with confidence in its value for the particular group for which it was first written, and with the hope that it may prove useful to others who have need of some knowledge of organic and biological chemistry, but who have only a limited amount of time to devote to that subject.

ALFRED VIVIAN

COLLEGE OF AGRICULTURE  
THE OHIO STATE UNIVERSITY  
COLUMBUS

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# FUNDAMENTALS OF ORGANIC AND BIOLOGICAL CHEMISTRY

## CHAPTER I

### INTRODUCTION

Biological chemistry is that branch of the study of living organisms which treats of their chemical composition and the changes the substances composing them undergo in the course of their life history. It deals with the sources of material and energy that are available to living organisms, and with the utilization of these sources in building up the bodies of plants and animals and in carrying on their characteristic activities.

Although the knowledge of this subject is still very far from complete, a great mass of information has been obtained, the presentation of which would be far beyond the scope of such a text as this; but an attempt will be made to give a general survey of the subject, emphasizing the fundamental principles that have been found to underlie the chemistry of plants and animals.

Before the changes occurring in living organisms



can be followed, it is necessary to know as completely as possible the nature and chemical properties of the compounds of which these organisms are composed. As many of these compounds are quite complex, and differ considerably from those met in the study of inorganic chemistry, the larger part of this text will be devoted to a discussion of them. The later chapters will deal with the changes they undergo during the development of plants and animals.

**Water.**—Water is the most abundant single constituent of living organisms. If fresh plant or animal material is dried at a temperature slightly above  $100^{\circ}$ , the water is evaporated and its amount may be determined. The amount of water present varies greatly with the individual organism, and with the conditions to which it has been subjected. The average amount in green plants is about 80 per cent, and in animals about 65 per cent. Aside from being so abundant, water has many important functions to perform, which will be discussed later.

**Minerals.**—On heating the dry residue from the moisture determination to a higher temperature, part of it burns, and a smaller part remains as the ash which is composed of a number of salts, principally sulfates, phosphates, and chlorides of calcium, magnesium, potassium, and sodium, together with smaller amounts of several other elements. The salts are obtained by plants from the soil, and by animals mostly from the plants they use as food. The very important functions which the mineral elements perform in living organisms will be mentioned as their uses become apparent.

The amount of ash in different plants and animals varies widely, but, as fair averages, 1.5 per cent for plants and 5.0 per cent for animals, may be given.

**Organic Substances.**—The substances that disappear on burning are those that are most characteristic of living organisms; they comprise about 18.5 per cent of plants, and about 30 per cent of animals, and they include a great variety of compounds, such as the fats and sugars, and many others of the same general nature. Analyses show that all of these substances contain carbon and hydrogen, most of them also contain oxygen, and some of them nitrogen. A few other elements in smaller amounts occur as constituents of some of these compounds.

**Organic Chemistry.**—For many years it was thought that these substances could be formed only through the agency of living organisms; for this reason their study was called Organic Chemistry. In 1828 Woehler succeeded in preparing one of these compounds from inorganic sources. Since this important synthesis, many more have been obtained in this way, and many other similar compounds, that have not been found in nature, also have been prepared. Thus the original meaning of the term Organic Chemistry has been lost, but the name still is used for a study of these substances.

Because of its universal occurrence in these compounds, and because it is the central element around which the others are grouped, carbon is the characteristic element in organic chemistry. In fact, this branch of chemistry is sometimes defined as the chem-

istry of the compounds of carbon. However, a few carbon compounds, such as carbon dioxide and the carbonates, are inorganic, so this definition is not exact. A great many compounds contain only carbon and hydrogen, and for this reason are called Hydrocarbons. All other organic compounds may be derived directly or indirectly from these hydrocarbons by appropriate chemical reactions. Organic chemistry may be defined more accurately, then, as the chemistry of the hydrocarbons and their derivatives.

**Relationships.**—The number of hydrocarbons is very large; many thousands of them are known. As each may give rise to a great many derivatives, the total number of organic compounds is immense. It would be hopeless to attempt to study each, even of the more important ones, individually. Fortunately they fall into large groups of compounds having similar properties, so that a knowledge of the chemistry of one of a group serves for all its members. Beside this, the various groups of compounds are related closely to each other. Thus an apparently impossible mass of facts is arranged in such an orderly way that their study becomes comparatively easy.

The organic compounds occurring in plants and animals are mostly quite complex. It will be necessary, therefore, to study the simpler members first, in order to gain a knowledge of their general nature and their relationships to each other. This information then may be applied to a study of the more complex substances which take part in the processes of plant and animal growth.

**First Principles.**—There are two facts which may be stated before the systematic study is begun: first, atoms of carbon have a remarkable tendency to combine with each other; this explains, in part at least, the great number of organic compounds that are known. Second, in all the compounds met in this work, carbon is tetravalent. That this central element of organic compounds undergoes no change in total valence in the reactions to be recorded, does much to simplify their study.



## CHAPTER II

### THE HYDROCARBONS

**Methane.**—Since all other organic compounds may be derived from the hydrocarbons, these substances form the natural starting point in a study of organic chemistry. As carbon is tetravalent and hydrogen monovalent, the molecule of the simplest possible hydrocarbon would contain one atom of carbon and four atoms of hydrogen. Its formula would be  $\text{CH}_4$ . In fact, this is a commonly occurring gas whose chemical name is methane.

**Occurrence.**—Methane is formed wherever plant or animal remains undergo decomposition in the absence of air. If the bottom of a marsh is stirred, bubbles of gas rise, which is composed largely of methane. Its formation in this case is due to the decay of leaves and other organic material that has accumulated at the bottom of the marsh. Because of its occurrence in such places, methane is sometimes called "marsh gas." Also, during the formation of the coal measures, methane was produced, and some of it was retained in the crevices between the layers of coal. When the coal is mined, this gas escapes and mixes with the air in the mine. In certain proportions, it

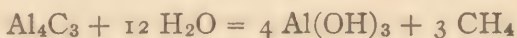
forms an explosive mixture with air, and such a mixture has caused many accidents. Because it is an easily combustible gas, methane is known to miners as "fire damp."

Although the method of formation of natural gas is not known definitely, it is quite probable that it was produced by the decay of plant or animal remains. At any rate a very large part of natural gas, over 90 per cent in most cases, is methane. Coal gas also contains as much as 40 per cent of this compound. Some methane is formed in the intestines, especially of herbivorous animals, by the action of bacteria on food residues. Small amounts of methane also occur in the air expired from the lungs.

**Preparation.**—There are several methods by which methane may be prepared. It is formed in an electric arc passing between carbon poles in an atmosphere of hydrogen. This method does not give a large yield, but is of interest because it proves that this organic compound may be formed by direct union of the elements composing it. A temperature of about  $1200^{\circ}$  must be reached before the reaction occurs.



Another inorganic source of methane is the action of water on aluminum carbide:



Methane may be formed conveniently in the laboratory by heating a dry mixture of an organic salt,

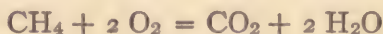
sodium acetate, and a strong alkali. The reaction may be represented by the following equation:



Soda lime is usually used instead of sodium hydroxide. The chemistry of this reaction will be considered somewhat later.

**Properties.**—Methane, like hydrogen, was long considered a permanent gas, but it is possible to liquefy it if a very high pressure and a low temperature are used. Liquid methane boils at  $-152^\circ$  and solidifies at  $-186^\circ$ . The gas is colorless, odorless, and tasteless.

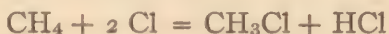
The most noticeable chemical property of methane is its extreme inactivity. Strong acids and alkalies, and such powerful oxidizing agents as chromic and permanganic acids have little effect on it. When heated to its kindling temperature in the presence of oxygen, however, methane burns very rapidly. Its combustion may be represented by the following equation:



The application of the gas laws to this reaction shows that two volumes of oxygen are required to burn one volume of methane. A mixture of the two gases in this proportion gives the most violent explosion. As air contains only about 20 per cent oxygen, five times as much of it as of oxygen is required to complete the reaction. In air, then, the most violent explosion is produced by a mixture of one volume of methane and ten volumes of air. No explosion occurs if less than

six or more than fourteen volumes of air are mixed with one volume of methane.

**The Action of Chlorine.**—If methane is mixed with chlorine and the mixture is exposed to diffuse light, chemical changes occur, the first of which is represented by the equation



An atom of chlorine has replaced an atom of hydrogen in the methane molecule. Such a change is called a substitution reaction, and the compound formed is a substitution product of methane, called mono-chlor-methane or methyl chloride. The reaction does not stop at the point indicated by the above equation, but each of the hydrogen atoms of the methane molecule in turn may be replaced by chlorine. The successive reactions may be expressed by the following equations:



The products of the above reactions are, respectively, di-chlor-methane, tri-chlor-methane or chloroform, and tetra-chlor-methane or carbon tetrachloride. The actual result of the reaction is a mixture of the four compounds given. The proportion in which they are formed depends on the relative amounts of methane and chlorine originally present. The individual com-

pounds may be separated from the mixture by appropriate means.

Bromine acts on methane in the same way as does chlorine, but much less readily. In this case, the mixture must be heated before substitution occurs. The bromine compounds are entirely analogous to those of chlorine, and are formed by the replacing of one, two, three, or four of the hydrogen atoms of methane by bromine. The compounds formed are  $\text{CH}_3\text{Br}$ , methyl bromide,  $\text{CH}_2\text{Br}_2$ , dibromomethane,  $\text{CHBr}_3$ , bromoform, and  $\text{CBr}_4$ , carbon tetrabromide.

The corresponding iodine compounds cannot be formed by the direct action of iodine on methane, but there are indirect methods by which they may be prepared.

**The Halogen Substitution Products of Methane.**  
—The physical properties of the halogen substitution products of methane change gradually with changes in composition, as is shown in the following table. The specific gravities of the two compounds which are gases at ordinary temperatures are compared with air, those of the liquids and solids with water. The melting points of the solid compounds are given.

X =	Cl		Br		I	
	b. p.	sp. gr.	b. p.	sp. gr.	b. p.	sp. gr.
$\text{CH}_3\text{X}$	$-24^\circ$	0.95	$4.5^\circ$	1.7	$45^\circ$	2.3
$\text{CH}_2\text{X}_2$	40	1.3	98.5	2.5	180	3.3
$\text{CHX}_3$	61	1.5	151	2.9	m. 119	
$\text{CX}_4$	76	1.6	189	.....	decomp.	4.3
			m. 92			



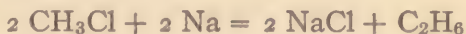
Methyl chloride,  $\text{CH}_3\text{Cl}$ , is manufactured from the residues from sugar beet molasses. It is used in the making of aniline dyes, and as a substitute for ammonia in producing low temperatures.

Chloroform,  $\text{CHCl}_3$ , is a sweetish smelling, rather heavy liquid. It is used commercially as a solvent for rubber and as a cleansing agent. In the laboratory it is very useful as a solvent for fats and other substances not soluble in water. It is valuable in surgery as an anesthetic. For this purpose it must be prepared very carefully. Pure chloroform is unsafe as an anesthetic because it decomposes slowly, especially when exposed to light and air, forming small amounts of chlorine and phosgene,  $\text{COCl}_2$ , both of which are irritating and poisonous gases. This decomposition is prevented by the addition of about 2 per cent of alcohol.

Iodoform,  $\text{CHI}_3$ , is a yellow, crystalline substance with a penetrating and persistent odor which is suggestive of a hospital. It is used as an antiseptic in the treatment of wounds.

Carbon tetrachloride,  $\text{CCl}_4$ , is a heavy, fairly volatile liquid. It is used to some extent commercially as a solvent for extracting fats from seeds. It is rather expensive for this purpose, and it is also too heavy to be used conveniently. The fact that it corrodes metals also makes its commercial use difficult. Its vapor is toxic to insects and since it is not inflammable, it is safer to use for fumigating than is carbon bisulfide. However, it is not volatile enough to be entirely satisfactory for this purpose. It is used in noninflammable cleaning fluids, and to some extent in fire extinguishers.

**Ethane.**—From a chemical point of view, the monohalogen substitution products of methane are the most interesting, because they are used frequently in the building up of more complex organic compounds. These substances are very much more active chemically than the hydrocarbon from which they are derived. A single example of this activity will be sufficient for the present. If methyl chloride is dissolved in ether and treated with metallic sodium, the following reaction occurs:



Another hydrocarbon called ethane has been formed.

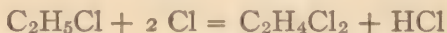
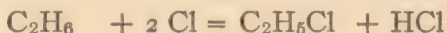
**Properties.**—Like methane, ethane is a colorless, odorless gas which occurs in very small quantities along with methane in natural gas. It is less soluble in water than is methane, and it is very much more easily liquefied. The liquid boils at  $-90^\circ$ . Its chemical properties are like those of methane. In general it is very inactive, but it burns readily when heated to its kindling temperature in the presence of oxygen, and it forms explosive mixtures with air. The products of its combustion are carbon dioxide and water.



There is a slight increase in volume when ethane is burned.

**The Action of Chlorine.**—Ethane is like methane in its behavior with chlorine. It is evident that many more substitution products are possible, since there are more hydrogen atoms to be replaced. As a matter of

fact, all the possible chlorine substitution products of ethane may be prepared. Since the reactions are entirely analogous to those with methane, only two of them will be given:



The first of these compounds is called ethyl chloride. It is a gas at ordinary temperatures, but liquefies at about  $12^\circ$ . It is manufactured by heating together alcohol, sulfuric acid, and potassium chloride. It is useful as a local anesthetic, since the liquid evaporates very rapidly and produces a low temperature. Ethyl bromide,  $\text{C}_2\text{H}_5\text{Br}$ , is also used as an anesthetic.

When the preparation of the second compound is attempted, it is found that two different substances are formed. Their composition and molecular weight correspond to the formula  $\text{C}_2\text{H}_4\text{Cl}_2$ . Their physical properties are quite different: one boils at  $84^\circ$  and has a specific gravity of 1.28; the other boils at  $58^\circ$  and its specific gravity is 1.17. Although their chemical properties are quite similar, they are not exactly the same.

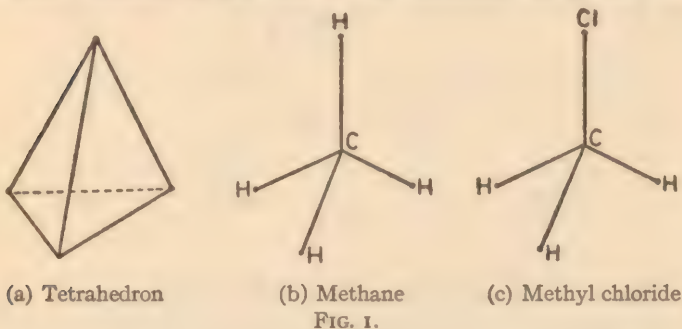
It is evident that the formula given for these compounds,  $\text{C}_2\text{H}_4\text{Cl}_2$ , indicating the kinds and number of atoms in their molecules, is not sufficient to distinguish them. There must be some differences that this formula does not show. It seems reasonable to suppose that the differences in the properties of these compounds may be due to differences in the arrangement of the atoms in the molecules. Molecules are too

small to be seen by any method known at present, so that no direct proof can be obtained on this point. However, there is a great deal of indirect evidence which points to a definite arrangement of atoms in molecules. This subject is so important that it will be worth while to go back a little, in order to gain the fundamental ideas of structure in organic compounds.

**The Structure of Methane.**—The first step in the action of chlorine on methane is the substitution of one chlorine atom for one of the four hydrogen atoms to form  $\text{CH}_3\text{Cl}$ , methyl chloride. There are many other ways in which methyl chloride may be prepared, but, no matter which method is used, the compound always has exactly the same properties. No second substance having the formula  $\text{CH}_3\text{Cl}$  ever has been found. It is possible to explain this fact in two different ways. Either one of the hydrogen atoms in the methane molecule is placed differently from the others, and for this reason is more easily replaced by chlorine, or all four of them are similarly placed, so that it makes no difference which is replaced. It can be shown experimentally that the latter is the true explanation. It is necessary, then, to picture some structure for methane, some arrangement of the five atoms in the molecule, such that the position of each of the hydrogen atoms is like that of all the others in respect to its relation both to the other hydrogen atoms and to the carbon atom with which all of them are combined. The arrangement which meets all these conditions best, and at the same time explains many other facts of organic chemistry, is based on the regular tetrahedron, an illustra-



tion of which is given in the accompanying diagram (Fig. 1, a). The carbon atom of methane is considered placed at the center of this figure, and one of the hydrogen atoms at each of the four vertices. The valences connecting the carbon atom with the hydrogen atoms are represented by lines reaching from the center of the figure to its vertices (Fig. 1, b). It is evident that the hydrogen atoms are arranged symmetrically around the carbon atom, so that each of them bears the same relation to the rest of the molecule as do all the



others. If one of the hydrogen atoms is replaced by chlorine, it makes no difference in which position it is placed, since any two figures so formed may be proven identical by superposition, the geometrical proof of identity. The same is true of the dichlorine, trichlorine, and tetrachlorine substitution products of methane,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$ . Only one compound having each of these formulas is known.

**The Structure of Ethane.**—In the reaction of methyl chloride with sodium, the chlorine atom is removed from each of two such molecules. This leaves



two groups of atoms,  $\text{CH}_3$ —, each of which has one free valence. These groups cannot exist free, but immediately combine with each other. This tendency of carbon atoms to combine with each other has been mentioned as one of the causes for the great number of carbon compounds. The compound formed by this union of two methyl groups is ethane. Its structure is shown in Fig. 2, a, in which only the lines representing the valences are given.

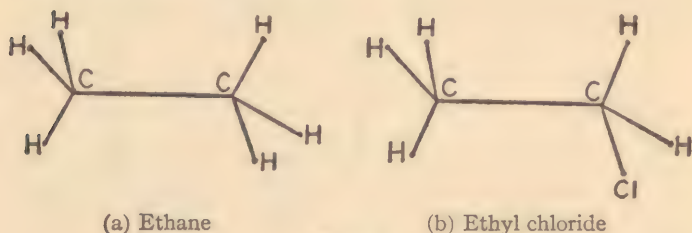


FIG. 2.

**The Chlorine Substitution Products.**—If one of the hydrogen atoms in the molecule of ethane is replaced by chlorine, only one arrangement is possible, since the two ends of the molecule are alike and each hydrogen atom bears the same relation to the rest of the molecule as do all the rest. From the structure (Fig. 2, b) it would seem that there could be only one monochlorethane, and, as a matter of fact, only one is known.

When a second chlorine atom is introduced, it might combine with the same carbon atom that holds the first, or with the other carbon atom. It is evident that the structures resulting are not the same. One is symmet-

rical and the other is not. It might be expected, then, that there would be two dichlorethanes. It has been stated, already, that two such compounds exist, and their properties have been given. It can be shown that the compound with the symmetrical formula is the one which boils at  $84^{\circ}$ . The structural formulas for these compounds are given in Fig. 3.

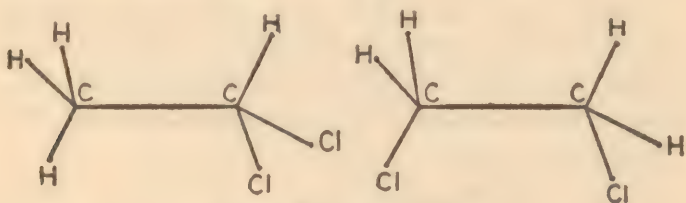
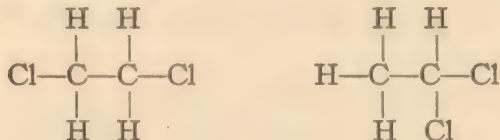


FIG. 3.—The Dichlorethanes.

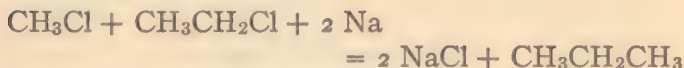
**Isomerism.**—Compounds which, like the two dichlorethanes, have the same percentage composition and the same molecular weight, but differ in structure and properties, are called isomers. The formula  $C_2H_4Cl_2$  is not sufficient to distinguish these compounds. It is necessary to indicate the arrangement of the atoms in the molecule. For frequent use it would be inconvenient to attempt to represent the tetrahedral structure on a plane surface, so it is customary to write the formulas as follows:



This, however, is not an accurate picture of the real structures. A more convenient method, which still is

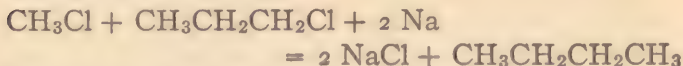
perfectly clear, is  $\text{CH}_2\text{ClCH}_2\text{Cl}$  and  $\text{CH}_3\text{CHCl}_2$ . It should be remembered, however, that these convenient ways of writing the formulas are only shorthand methods of expressing the structures given in Fig. 3. With this understood, it is only necessary to write the formulas in such a way that there can be no question which structure is meant.

**Synthesis of Propane.**—The reaction of methyl chloride with sodium has been given. If, instead of methyl chloride, a mixture of that compound with ethyl chloride is used, the following is among the changes that occur:



The new hydrocarbon formed is propane. It is a gas which is more easily liquefied than either methane or ethane. The liquid boils at  $-17^\circ$ . The chemical properties of propane are like those of methane and ethane. In general it is very inactive, but it burns readily in air when heated to its kindling temperature, and one or more of its hydrogen atoms may be replaced by chlorine.

**Synthesis of Butane.**—If a mixture of the monochlorine substitution product of propane and methyl chloride is treated with sodium, changes like those just given occur:



The hydrocarbon produced in this case is butane, another gas which may be liquefied at  $0^\circ$ , and whose

chemical properties are like those of the hydrocarbons already described.

**The Paraffin Series of Hydrocarbons.**—If the details of the chemical method used are left out, each of the hydrocarbons so far discussed may be considered as derived from the preceding one by the substitution of a  $\text{CH}_3$ — group for an atom of hydrogen. Thus if one hydrogen is removed from methane,  $\text{CH}_3$ — is left. If a  $\text{CH}_3$ — group is added to this,  $\text{CH}_3\text{CH}_3$  or ethane is formed. If a hydrogen atom is removed from ethane, the monovalent group  $\text{CH}_3\text{CH}_2$ — remains. If the monovalent group  $\text{CH}_3$ — combines with this,  $\text{CH}_3\text{CH}_2\text{CH}_3$  or propane, is formed. This process might be continued indefinitely. The products form a series of hydrocarbons related to each other in composition and structure as has just been described. In fact, the members of this series are known at least as far as  $\text{C}_{60}\text{H}_{122}$ , hexacontane.

**Properties.**—The physical properties of these compounds change gradually with change in molecular weight, as is shown in the following table which gives the formulas and boiling points of the first few members of the series:

Name	Formula	Boiling Point	Name	Formula	Boiling Point
Methane..	$\text{CH}_4$	$-152^\circ$	Hexane....	$\text{C}_6\text{H}_{14}$	$70^\circ$
Ethane....	$\text{C}_2\text{H}_6$	$-90$	Heptane...	$\text{C}_7\text{H}_{16}$	98
Propane...	$\text{C}_3\text{H}_8$	$-17$	Octane....	$\text{C}_8\text{H}_{18}$	126
Butane....	$\text{C}_4\text{H}_{10}$	$\square$	Nonane....	$\text{C}_9\text{H}_{20}$	150
Pentane...	$\text{C}_5\text{H}_{12}$	36	Decane....	$\text{C}_{10}\text{H}_{22}$	173

Of the whole series, the first four are gases. The members from  $C_5H_{12}$  to  $C_{16}H_{34}$  are liquids, whose boiling points rise with increase in molecular weight. The higher members are solids, whose melting points rise with increased molecular weight.

The chemical properties of all the members are the same. All are very inactive. For this reason they are called the "Paraffin Hydrocarbons." All of them burn readily in air when heated to their kindling temperature, and all of them are acted on by chlorine, forming substitution products.

**Homologous Series.**—The composition of the whole series may be represented by a single formula,  $C_nH_{2n+2}$ , in which  $n$  represents the number of carbon atoms in the molecule. This is called the general formula of the series. Each member differs from the one next it in composition, by one atom of carbon and two atoms of hydrogen.  $CH_2$  is, then, the common difference of the series.

A series of compounds related to each other in composition and structure as are the paraffin hydrocarbons, whose chemical properties are practically identical, and whose physical properties change gradually with changes in molecular weight, is called an homologous series. As was stated earlier, the grouping of organic compounds into series, all of whose members have the same chemical properties, simplifies their study immensely.

**Occurrence and Uses of the Paraffin Hydrocarbons.**—The paraffin hydrocarbons occur very rarely in plants and animals, and they are of slight physio-



logical importance. However, they are of very great practical value. The occurrence of methane as the principal constituent of natural gas has been mentioned. Others of the lower members of the series occur with it in small amounts.

The petroleum of the Pennsylvania and neighboring oil fields is composed almost entirely of the liquid members of this series, in which the gaseous and solid members are dissolved. The oils of other regions also contain some paraffin hydrocarbons, but along with them a greater or less amount of hydrocarbons of other series. All these petroleums contain some impurities, many of which must be removed before the oil is fit for use. Solid masses of hydrocarbons are found both in Europe and in this country. The bitumens and asphalts, which are used very extensively for paving and roofing, are composed largely of other hydrocarbons, but contain some of the paraffin series.

Petroleum oil is used to some extent directly as a fuel in especially constructed burners, but most of it is separated into various parts by fractional distillation. These fractions are used for widely different purposes.

The gaseous members, which come over first, are sometimes collected and used instead of ammonia in the manufacture of ice. The portion distilling between  $40^{\circ}$  and  $80^{\circ}$  may be separated into two or more fractions, but these are used for very much the same purposes: the dry cleaning of clothes, the solution of fats and similar substances in the laboratory, and the com-

mercial extraction of fats and oils from those seeds in which they are contained in large amounts.

The fraction collected between  $80^{\circ}$  and  $150^{\circ}$  is gasoline. Because of its use in internal combustion engines, this portion is in the greatest demand at present. Between  $150^{\circ}$  and  $300^{\circ}$  kerosene is collected. Many different grades of this product, depending on the color and temperature of ignition, are on the market. All these fractions are treated with sulfuric acid and sodium hydroxide in order to remove basic and acid impurities which would interfere with their use.

The residue is separated into liquid and solid portions, although there is no very sharp line between them. The liquid and softer part, with more or less purification, furnishes paraffin oil, lubricating oils, and vaseline. The solid portion is purified and crystallized in the form of paraffin. Large amounts of this substance are used in candle making, in finishing cloth and paper of certain kinds, in impregnating matches, in extracting perfumes from flowers, in sealing foods, and in many other ways.

The immense demand for gasoline in the last few years has led to many attempts to increase the yield of this important fraction. One method by which this is done is called "cracking." After the lower boiling fractions have been removed, the distillate is allowed to drop back into the heated liquid. By this means the distillate is heated quickly to a high temperature. The large molecules are decomposed into smaller ones which, of course, have a lower boiling point. With this improvement it is possible to obtain a yield of burning

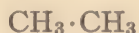
oils, including kerosene, of from 78 to 80 per cent of the crude petroleum.

Some of the liquid hydrocarbons are present in natural gas in much the same way as water vapor is held in the air. These may be removed by subjecting the gas to high pressure. From some of the California gas wells as much as three gallons of this "casinghead gas" are obtained from 1000 cubic feet of gas. This is very low boiling material, and is blended with the higher boiling fractions before being used in engines. The low boiling liquid hydrocarbons may also be removed from gas by passing it through liquid hydrocarbons of higher boiling point, in which the low boiling liquids carried by the gas are dissolved or absorbed.

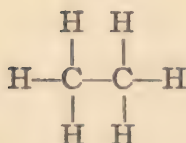
Many attempts have been made to use kerosene in internal combustion engines. These have met with partial success, but the difficulties in the way of using a high boiling liquid have not been overcome sufficiently to make its use at all general as yet.

**Isomerism of the Paraffin Hydrocarbons.**—As has been stated, each member of the paraffin series of hydrocarbons may be considered derived from the one preceding it by replacing one of the hydrogen atoms of the simpler compound by a  $\text{CH}_3$ — group, just as the monochlorine substitution products are formed by replacing one of the hydrogen atoms by chlorine. Since in the molecules of methane and ethane, all the hydrogen atoms are similarly placed, it makes no difference in which position the  $\text{CH}_3$ — group is inserted. Only

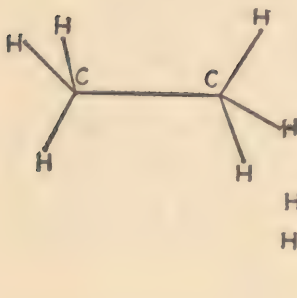
the one formula, given below, can be written for ethane, and only one for propane.



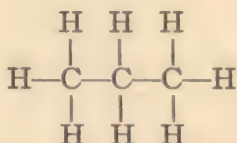
or



or



or



or

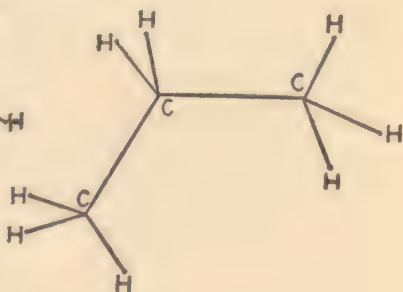
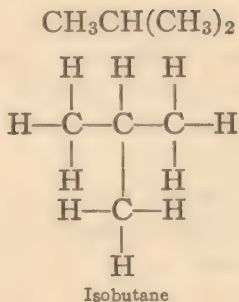
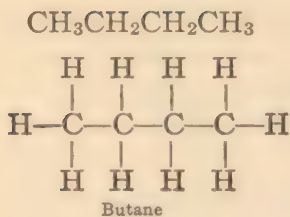


FIG. 4.

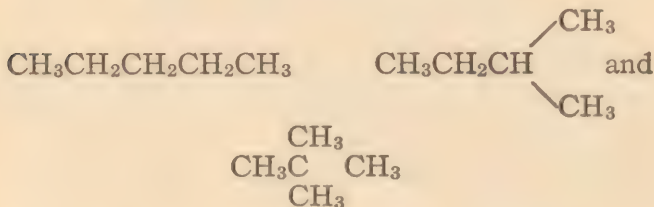
As might be expected, only one compound having each of these formulas is known.

When the next member of the series is formed, however, the  $\text{CH}_3$ — group may replace a hydrogen atom attached to one of the end carbon atoms, or it may replace a hydrogen atom attached to the middle carbon atom of propane. The compounds resulting are illustrated in the following formulas:



These two formulas appear quite different, and it might be supposed that they represent different compounds. In fact, both of them are known. The "straight chain" compound is normal butane, a gas which liquefies at  $0^\circ$ ; the "branched chain" one is isobutane, which liquefies at  $-17^\circ$ .

A study of the structure of the two butanes shows that there are three, and only three, different places in which a  $\text{CH}_3-$  group may be inserted. In this way the following formulas for the pentanes are derived:

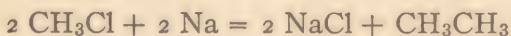


It is evident that, as the number of carbon atoms in the molecule increases, the number of possible arrangements increases very rapidly. Thus there are five hexanes and nine heptanes, and the possible isomers of

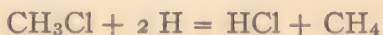


the compound  $C_{13}H_{28}$  are 802. When it is remembered that each of these hydrocarbons may form several different chlorine substitution products, one of the reasons for the great number of organic compounds becomes apparent.

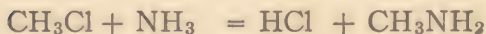
**Properties of Methyl Chloride.**—Because of their frequent use in the synthesis of other compounds in the laboratory, those chlorine substitution products, in which only one of the hydrogen atoms of the hydrocarbon has been replaced by chlorine, are of particular interest. It was stated that these compounds are much more active chemically than the hydrocarbons from which they are derived. Only one of the reactions of methyl chloride was given, that with sodium:



When treated with nascent hydrogen, the following change takes place:



By both of these means, then, it is possible to form a hydrocarbon from methyl chloride. The following three reactions resemble very closely the double decomposition reactions of inorganic chemistry:

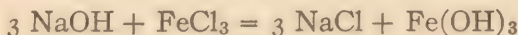


The product of the first of these reactions is called a cyanide or nitrile; that of the second, an amine; and that of the third, an alcohol. Each of these groups of substances will be discussed later.

**Radicals.**—It will be noticed that the  $\text{CH}_3$ —group goes through these reactions unchanged, in much the same way that the  $\text{SO}_4$  group goes through the following reaction:

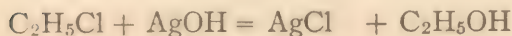
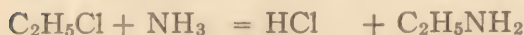
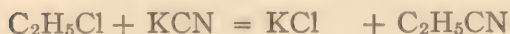
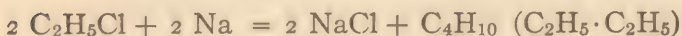


or the OH group through the following:



Such groups of atoms are called radicals. Thus  $\text{CH}_3$ — is a monovalent radical, and it has been named Methyl. The products of the reactions of methyl chloride just given are methyl cyanide, methyl amine, and methyl alcohol.

**Ethyl Chloride.**—The monochlorine substitution product of ethane,  $\text{C}_2\text{H}_5\text{Cl}$ , undergoes reactions similar to those just given for methyl chloride. They are indicated in the following equations:



It is evident that the monovalent group  $C_2H_5-$  acts in the same way as does the radical  $CH_3-$ . The  $C_2H_5-$  radical is called Ethyl. The combination of two ethyl groups results in the formation of the hydrocarbon butane. The addition of hydrogen to ethyl gives ethane. The compounds formed by the last three reactions are, respectively, ethyl cyanide, ethyl amine, and ethyl alcohol.

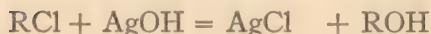
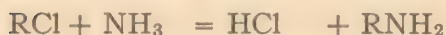
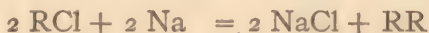
**Alkyl Radicals.**—Reactions like those just given for methyl chloride and ethyl chloride take place with the monochlorine substitution products of all of the paraffin hydrocarbons. In each case a monovalent radical, containing one less hydrogen atom than the hydrocarbon, takes the same part in the reactions as the methyl and ethyl radicals do in those given above. The general term Alkyl Radical has been applied to all the monovalent radicals formed by removing one atom of hydrogen from the paraffin hydrocarbons. Since the general formula for the paraffin hydrocarbons is  $C_nH_{2n+2}$ , that for the alkyl radicals is  $C_nH_{2n+1}$ . It is more usual to use the letter R to represent any of the alkyl radicals. Thus the general formula for the monochlorine substitution products of the paraffin hydrocarbons is,  $C_nH_{2n+1}Cl$ , or  $RCl$ .

**The Monochlorine Substitution Products.**—The monochlorine substitution products of the paraffin hydrocarbons form an homologous series, just as do the hydrocarbons themselves. The general formula for the series has been given above. The physical properties of the series change gradually with change in molecular weight, as is shown in the following table,

in which the boiling points of the first few members of the series are given:

Formula	Boiling Point	Formula	Boiling Point
CH <sub>3</sub> Cl	-24°	C <sub>5</sub> H <sub>11</sub> Cl	107°
C <sub>2</sub> H <sub>5</sub> Cl	12	C <sub>6</sub> H <sub>13</sub> Cl	133
C <sub>3</sub> H <sub>7</sub> Cl	47	C <sub>7</sub> H <sub>15</sub> Cl	159
C <sub>4</sub> H <sub>9</sub> Cl	78		

All the members of the series have the same chemical properties as have been given for methyl chloride and ethyl chloride. The equations for these reactions are repeated below in their general form:



It will be seen that the products of the first two reactions, RR and RH, are hydrocarbons, and that these reactions are general methods by which hydrocarbons may be formed from monochlorine substitution products. The second gives rise to the hydrocarbon having the same number of carbon atoms as the substitution product, and the first gives rise to the hydrocarbon containing twice as many carbon atoms.

In these few equations are summarized the chemical properties of a large number of compounds.

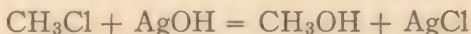
Bromine and iodine form similar series of mono-substitution products, whose general formulas are, respectively,  $RBr$  and  $RI$ . The chemical properties of these series of compounds are the same as those just given for the chlorine substitution products.



## CHAPTER III

### THE ALCOHOLS AND ETHERS

**Methyl Alcohol.**—The reaction between methyl chloride and silver hydroxide is one of the methods for preparing methyl alcohol:

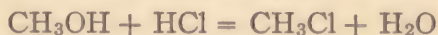


Methyl alcohol is a colorless liquid which boils at  $64.5^\circ$  and has a specific gravity of 0.812 at  $0^\circ$ . When pure, it has a rather pleasant odor, but it often contains impurities which give it a disagreeable smell. It mixes with water in all proportions. It burns with a nonluminous flame. It is poisonous, affecting the eyes and sometimes causing blindness. In nature it occurs combined in oil of wintergreen, in the substance pectin, which causes the juices of certain fruits and vegetables to set to a jelly, and in many other compounds.

**Preparation and Uses.**—Methyl alcohol is prepared commercially by heating wood in the absence of air. This is called destructive distillation. During the heating a large amount of liquid products distills over. On standing, these separate into two layers, one an oily substance called wood tar, the

other an aqueous layer, pyroligneous acid. The solid residue of the wood is charcoal. The watery layer contains several compounds, among which the most important are methyl alcohol, acetone, and acetic acid. This is the principal commercial source of methyl alcohol, which for that reason is often called wood alcohol or wood spirit. The principal uses of methyl alcohol are as a solvent in the laboratory and in the manufacture of such products as varnishes and celluloid, as a denaturant for ordinary alcohol, and as a reagent in the manufacture of certain dyes.

**Properties.**—In its structure, methyl alcohol resembles the inorganic hydroxides, such as sodium hydroxide. In fact, it has some basic properties, but it is a very weak base, not strong enough to turn red litmus blue. Its basic properties are shown by its reaction with hydrochloric acid:



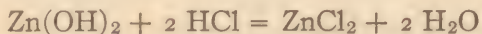
At first sight, this reaction appears entirely analogous to the neutralization of sodium hydroxide by hydrochloric acid, but it differs in one important respect. Sodium hydroxide is highly dissociated in solution, and it reacts with hydrochloric acid instantaneously. Methyl alcohol is only very slightly dissociated, if at all, and it reacts with hydrochloric acid very slowly.

With phosphorus pentachloride, the following reaction occurs:

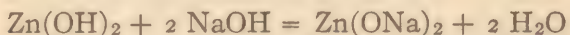


The production of hydrochloric acid in this reaction is used as a test for the presence of the hydroxyl group in organic compounds. Both of these are methods by which chlorine substitution products may be formed from alcohols.

There are certain inorganic hydroxides which may act either as acids or bases, depending on the conditions to which they are subjected. Thus, zinc hydroxide acts as a base when treated with hydrochloric acid:



But if sodium hydroxide acts on zinc hydroxide, the latter compound acts as an acid. The hydrogens of the hydroxyl groups are replaced by sodium, and sodium zincate is formed:

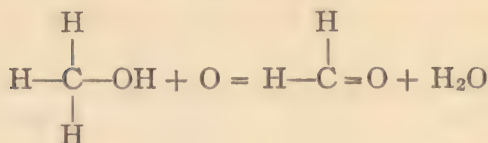


Methyl alcohol does not react with sodium hydroxide in this way, but, if it is treated with metallic sodium, the hydrogen of the hydroxyl group is replaced:



This is very much like the action of sodium on water. The compound formed, sodium methylate, is strongly basic, and is very active chemically.

When ignited in the presence of oxygen, methyl alcohol burns to carbon dioxide and water. If milder oxidizing agents are used, it is only partially oxidized to formaldehyde:



The hydrogen atom of the hydroxyl group and one of those combined with the carbon atom are removed, and a double bond is formed between the carbon and oxygen atoms.

**The Determination of Structure.**—Methyl alcohol furnishes an excellent illustration of the methods that are used for determining the structure of organic compounds. The first step necessary is the purification of the compound to be studied. This is usually accomplished by fractional distillation or crystallization, depending on the physical properties of the substance. The next step is the determination of its composition by analysis. If the unknown were methyl alcohol, the results of the analysis would be: carbon, 37.5 per cent; hydrogen, 12.5 per cent; oxygen, 50.0 per cent. This gives the proportion by weight in which the three elements enter into the composition of the compound. It is also necessary to know the relative number of atoms of each of the elements present. These ratios may be found by dividing the per cent of each element in the compound by its atomic weight. The results in this case are as follows:

$$\text{Carbon, } 37.5 \div 12 = 3.125$$

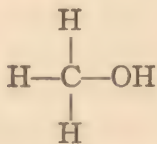
$$\text{Hydrogen, } 12.5 \div 1 = 12.5$$

$$\text{Oxygen, } 50.0 \div 16 = 3.125$$

The simplest possible formula for the compound is found by dividing these ratios by their greatest common divisor, which in this case is 3.125. The results are, carbon, 1; hydrogen, 4; oxygen, 1. The simplest formula which represents the composition of this compound is, then,  $\text{CH}_4\text{O}$ .

Whether this, or some multiple of it, is the correct formula is found by determining the molecular weight by one of a number of different methods. In this case the molecular weight would be found to be 32. Since this is the sum of the weights of the atoms in the formula just given, it follows that this formula is the correct one.

This tells the kind and number of the atoms in the molecule, but not the way in which they are arranged. The chemical reactions the substance will undergo must be relied on for evidence on this point. The reaction of  $\text{CH}_4\text{O}$  with sodium shows at once that one of the hydrogens is placed differently from the others, since one, and only one, of the hydrogens can be replaced by sodium. The reactions with hydrochloric acid and phosphorus pentachloride show that an hydroxyl group is present. These reactions make it seem probable that the formula for this compound is



Final proof can be obtained only by building up a compound of the supposed structure from compounds



of known structure. In this case the reaction of methyl chloride with silver hydroxide might be used:



If the compound obtained is identical in composition and properties with the compound being studied, the supposed formula is proven to be the correct one. With more complex compounds, of course, the problem is more difficult. These methods have been employed in determining the structure of thousands of organic compounds, and are being applied to the many new compounds that are being discovered each year.

**Ethyl Alcohol.**—Ethyl alcohol is derived from ethyl chloride in the same way as is methyl alcohol from methyl chloride:



It is a colorless, pleasant smelling liquid, lighter than water, with which it mixes in all proportions. It boils at  $78^\circ$ . Because of its very low freezing point,  $-130^\circ$ , it is sometimes used in thermometers which are intended to measure temperatures lower than  $-40^\circ$ , the freezing point of mercury.

In small amounts, ethyl alcohol occurs very widely distributed in nature. This is due to the fact that it is produced by the action of certain yeasts on grape sugar. The changes produced may be represented by the following equation:



This is called fermentation. It liberates a small amount of energy which the yeast plant may use. Since yeasts and sugar are almost universally distributed, it is not surprising that alcohol is found almost everywhere. Alcoholic fermentation was known very early in human history, and the use of fermented liquids as beverages dates back to prehistoric times. In the raising of bread with yeast, the change just mentioned occurs. Small amounts of sugar in the dough are acted on by the yeast with the production of alcohol and carbon dioxide. The carbon dioxide is kept from escaping by the tenacious dough, which becomes porous as the gas accumulates and expands.

**Commercial Preparation.**—Fermentation is the method by which ethyl alcohol is prepared commercially. The sugar required is usually prepared from starch. In this country corn starch is the common source, but in some European countries potato starch is used. Sugar may also be prepared from many other substances, among them wood. This has been proposed as a method for utilizing sawdust, "sulfite liquor" from the manufacture of paper from wood, and many other materials that now go to waste. The production of sugar from these substances by the methods in use at present is so difficult and expensive that they have not come into very general use. It seems quite likely, however, that these difficulties will be overcome, and that such materials will furnish an important source of alcohol.

As is often the case with living organisms, the products formed by the activity of yeast become toxic

as they accumulate, and stop the activity of the plant. For this reason it is not possible to produce a very concentrated solution of alcohol by fermentation. Not more than a 14 per cent solution can be produced, and it is probable that even this concentration is reached quite rarely. The alcohol is purified by distillation. After repeating the distillation several times, a mixture of 95 per cent alcohol and 5 per cent water is obtained. As this mixture distils at a constant temperature, no further separation can be effected by this means. Alcohol of this composition is used for most purposes without further purification. Pure or "absolute" alcohol may be prepared by removing the water from 95 per cent alcohol by means of some powerful dehydrating agent, such as calcium oxide. To be kept absolute, alcohol must be preserved carefully, as it takes up water from the air.

**Uses.**—For ages alcohol has been used in beverages. In small amounts, it has a stimulating effect, and for this reason it is sometimes valuable as a medicine. Otherwise, it certainly is not necessary, and is very likely to be harmful. The fact that alcohol may be used as a beverage makes it necessary to regulate very strictly its use for other purposes. For many of the most important uses of alcohol, it is not necessary that it should be pure. Certain substances may be added which make it unfit for drinking but do not impair its usefulness for other purposes. Alcohol treated in this way is said to be "denatured." The usual method is the addition of 10 per cent of methyl alcohol, and often small amounts of paraffin oils or

pyridine, a nitrogen-containing compound which has a very offensive odor.

Alcohol is indispensable in the laboratory as a solvent and reagent. It is also used commercially in large amounts in the manufacture of varnishes, dyestuffs, cellulose derivatives, and medicines, and in the preparation of flavoring extracts. It seems possible that in time it may take the place of gasoline as a source of power in internal combustion engines. Although its fuel value is not quite as high as that of gasoline, it requires less air in the mixture, has a cooler cycle, and may be compressed more highly. At present alcohol is not produced at a price which allows it to compete with gasoline, but, with improvements in its manufacture, and the probable continued increases in the price of gasoline, it is possible that in the future it may very largely take the place of gasoline. It has the advantage that it is made from materials whose supply is renewed each year, while the supply of petroleum is limited, and will undoubtedly be exhausted if the increase in its use continues at the present rate.

**The Alcohol Series.**—Methyl and ethyl alcohols are the first and most important members of an homologous series of alcohols, which are derived from the corresponding monochlorine substitution products of the paraffin hydrocarbons by replacing the chlorine atom by the hydroxyl group. The general formula of this series is  $C_nH_{2n+1}OH$ , or  $ROH$ , in which  $R$  may be any of the alkyl radicals. To distinguish them from certain other alcohols whose structure will be discussed later, the general formula may be written

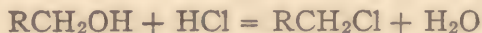


$\text{RCH}_2\text{OH}$ , in which R may represent H (in the case of methyl alcohol) or any of the alkyl radicals.

Several of the higher members of this series occur naturally in small amounts. Some of those of lower molecular weight are found in the compounds which give some fruits their characteristic flavors, and some of the higher members in the compounds known as the waxes. Propyl alcohol,  $\text{C}_3\text{H}_7\text{OH}$ , butyl alcohol,  $\text{C}_4\text{H}_9\text{OH}$ , and amyl alcohol,  $\text{C}_5\text{H}_{11}\text{OH}$ , are products of certain types of fermentation. The last mentioned is used to some extent commercially, and butyl alcohol promises to become a useful solvent when it is produced in larger quantities.

The first ten members of the series are liquids whose boiling points rise with increase in molecular weight. Methyl, ethyl, and propyl alcohols are miscible with water in all proportions. Above these the solubility decreases very rapidly. Amyl alcohol is very slightly soluble in water. The higher members of the series are white, waxlike solids, insoluble in water.

**Chemical Properties of the Alcohols.**—The chemical properties of the alcohols have been given under methyl alcohol. The reactions will be repeated here in their general form to show that they are common to all the alcohols. With hydrochloric acid the corresponding chlorine substitution product is formed:



The method of formation of this compound makes it seem very much like a salt. These "salts" formed by



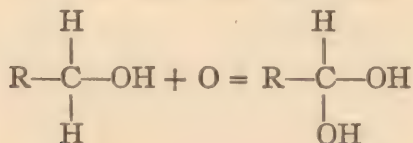
the action of an acid on an alcohol are called "Esters." They differ from the true salts in being very slightly, if at all, dissociated in solution. Similar compounds are formed by the action of other acids, such as hydrobromic, nitric, and sulfuric acids, on alcohols.

With phosphorus pentachloride and with sodium, the alcohols react as is shown in the following equations:



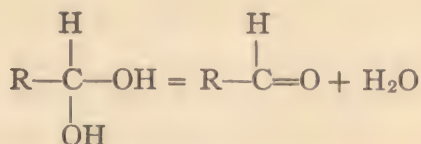
The former reaction serves as a test for the presence of the hydroxyl group in organic compounds, and as a general method for the preparation of the monochlorine substitution products. The latter shows that the hydrogen of the hydroxyl group is slightly acid in character.

The oxidation of an alcohol to an aldehyde probably takes place in two steps. In the first, the oxygen enters the molecule between a hydrogen atom and the carbon to which the hydroxyl group is attached:



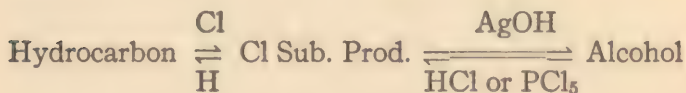
Compounds in which two hydroxyl groups are attached to the same carbon atom are unstable, and decompose

with the loss of a molecule of water. Aldehyde is formed in this case:



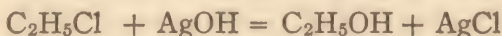
**Relationships of the Three Groups.**—So far, three large groups of organic compounds have been studied: the paraffin hydrocarbons, their monochlorine substitution products, and the alcohols. In each of these groups the chemical properties of all the members are the same. It is possible, then, to summarize the chemistry of a large number of compounds in a few reactions, as has been done in each case.

It is evident, also, that the three groups are very closely related to each other, as shown in the following outline:

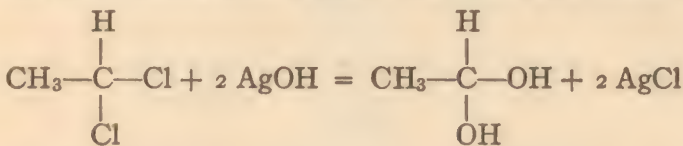


Thus it is possible to start with any member of any of the series and prepare the corresponding member of either of the other series. It will be remembered that, when a chlorine substitution product is treated with sodium, a hydrocarbon higher than the one in which the chlorine was substituted is formed. Using this reaction, it is possible to start with methane and prepare any member of any of the three series. As an

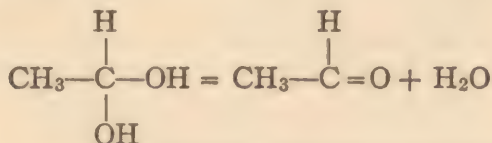
example, the reactions for the preparation of ethyl alcohol from methane will be given:



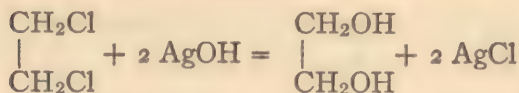
**Polyhydric Alcohols.**—If dichlorethane is treated with silver hydroxide, the product obtained depends on which of the two compounds of this name is used. In case the one having both chlorine atoms attached to the same carbon atom is taken, the result is as follows:



This product is the same as the one resulting from the first step in the oxidation of ethyl alcohol. Because two hydroxyl groups are attached to the same carbon atom, the compound is unstable. It loses one molecule of water and the corresponding aldehyde is formed:

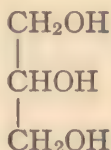


But if the dichlorethane in which each chlorine atom is combined with a different carbon atom is used, a stable alcohol is formed:



The product of this reaction is glycol. It is a thick, sweetish tasting liquid which occurs quite rarely in nature, but is found in small amounts combined in certain waxes. Each of the alcohol groups in the molecule may undergo all the reactions that have been given for the alcohols.

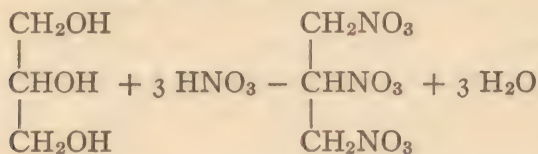
A similar compound, derived in the same way from the trichlorine substitution product of propane, contains three hydroxyl groups, each combined with a different carbon atom. Its formula is:



This alcohol is called glycerol, or, more commonly, glycerin. When pure it is a colorless, crystalline solid, melting at  $17^\circ$ . It mixes with water in all proportions. As usually prepared, it is a thick liquid with a sweet taste, and heavier than water. Glycerin is a constituent of all the fats which occur very widely distributed in nature. It is prepared commercially from this source. It is used as a solvent and reagent in the laboratory, is incorporated in some soaps, and is used as a medicine.

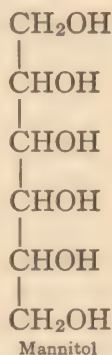
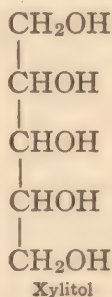
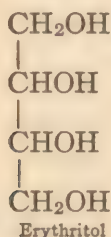
When glycerol is treated with  $\text{HNO}_3$ , the trinitrate is formed, very much as the trinitrate of iron is formed

when  $\text{Fe}(\text{OH})_3$  is treated with  $\text{HNO}_3$ , except that the former reaction goes very much more slowly:



The product of this reaction is glyceryl nitrate or nitroglycerin, as it is called more commonly, though incorrectly. It is a liquid which is an important constituent of explosives. Dynamite is made by mixing this substance with some absorbing material and molding it into sticks. Blasting gelatin and other high explosives are made by mixing nitroglycerin with nitrocellulose.

The formulas for some alcohols containing more than three hydroxyl groups are given below:



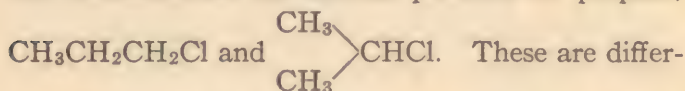
All of these occur in small amounts in various plants. The last named is abundant in certain fungi, and is closely related to the sugars.

Alcohols containing more than one hydroxyl group

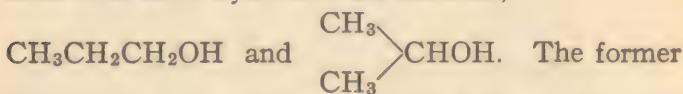


are called polyhydric alcohols. They are grouped according to the number of hydroxyl groups present. Thus glycerol is a trihydric alcohol and mannitol is a hexahydric alcohol. Since two hydroxyl groups cannot be combined with the same carbon atom, it is evident that any alcohol will contain at least as many carbon atoms as hydroxyl groups.

**Isomerism of the Monohydric Alcohols.**—As has been stated, the monohydric alcohols may be prepared by treating the monochlorine substitution products of the paraffin hydrocarbons with silver hydroxide. Since there is only one monochlorethane, only one alcohol having the formula  $\text{CH}_3\text{CH}_2\text{OH}$  is possible. There are two monochlorine substitution products of propane,



ent compounds, and the alcohols formed by treating them with silver hydroxide are different,

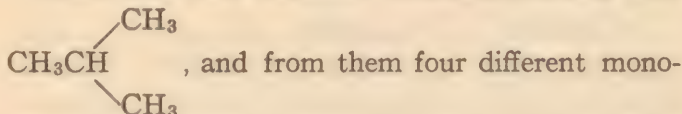


corresponds to the general formula which has been given for the alcohols,  $\text{RCH}_2\text{OH}$ . Such compounds are called primary alcohols, and are characterized by the monovalent group  $-\text{CH}_2\text{OH}$ . Stated in another way, they are alcohols in which two hydrogen atoms are combined with the carbon atom which holds the hydroxyl group. The second of the propyl alcohols does not contain this group, but instead the divalent

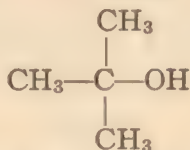
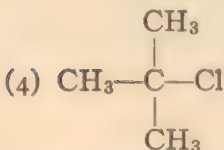
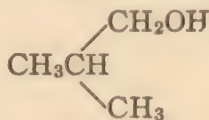
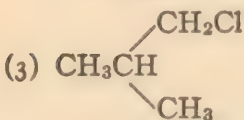
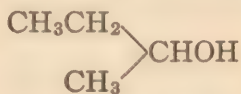
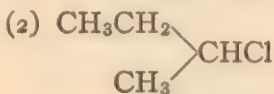
group,  $\begin{array}{c} \diagup \\ \text{CH} \\ \diagdown \end{array} \text{CHOH}$ , which is combined with two alkyl

radicals. The carbon atom with which the hydroxyl group is combined is also combined with only one hydrogen atom. This is similar to the middle alcohol group of glycerol, and is characteristic of the secondary alcohols. The general formula for the secondary alcohols is  $R_2CHOH$ . The two alkyl radicals may be the same or different.

There are two butanes,  $CH_3CH_2CH_2CH_3$  and



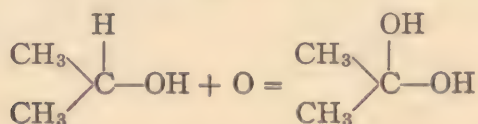
chlorine substitution products may be prepared. From each of these a monohydric alcohol may be formed by treating with silver hydroxide. The formulas for these chlorine substitution products and the corresponding alcohols are given below:



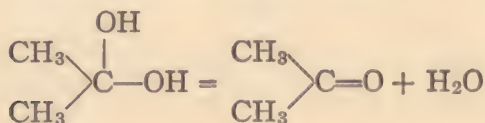
Of these alcohols, the first and third are primary, and the second is a secondary alcohol. The fourth does not

belong to either of these groups. The carbon atom with which the hydroxyl group is combined is not combined directly with any hydrogen atoms. It is characterized by the trivalent group  $\begin{array}{c} | \\ -\text{COH} \end{array}$ . Such compounds are called tertiary alcohols. Their general formula is  $\text{R}_3\text{COH}$ . The three radicals may be the same or different.

**Differences in Properties.**—In most of their properties, primary, secondary, and tertiary alcohols are alike. They differ, however, in the products of their oxidation. The formation of an aldehyde by the oxidation of a primary alcohol has been discussed. If secondary propyl alcohol is oxidized, the reaction proceeds in the same way. The first step is the introduction of oxygen between a hydrogen atom and the carbon with which the hydroxyl group is combined:



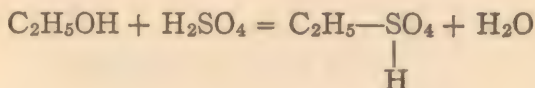
This compound is unstable because two hydroxyl groups are combined with the same carbon atom. A molecule of water is lost and a double bond is formed between the carbon and oxygen atoms:



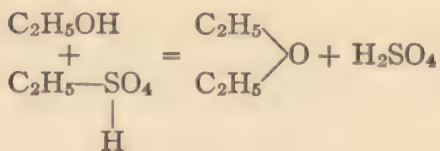
Acetone, the product of this reaction, is quite similar to the aldehyde formed by the oxidation of ethyl alcohol, but the two compounds are not identical. Acetone is a member of a group of compounds called ketones. It will be noticed that this compound differs from the aldehyde mentioned in having no hydrogen atom combined with the carbon atom with which the oxygen is combined.

From the structure of tertiary butyl alcohol, number 4 in the above list, it is evident that there is no hydrogen atom combined with the carbon atom holding the hydroxyl group. It is impossible, then, for it to form an intermediate compound like those produced by the oxidation of primary and secondary alcohols. This alcohol is not as easily oxidized as the primary and secondary alcohols. When oxidation does occur the molecule is decomposed, and no product is formed having as many carbon atoms in the molecule as the original alcohol.

**Ethyl Ether.**—On page 41 it was stated that alcohols form esters with acids other than hydrochloric. If sulfuric acid and ethyl alcohol are mixed and heated, an ester is formed by the alcohol and one of the acid hydrogens of the acid:



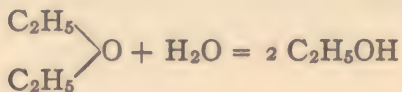
If more alcohol is added to this mixture, and the heating is continued, the sulfuric acid is regenerated, and an anhydride of the alcohol is formed:



The product bears the same relation to ethyl alcohol that sodium oxide,  $\text{Na}_2\text{O}$ , bears to sodium hydroxide,  $\text{NaOH}$ . In other words, it is ethyl oxide, though it is usually called ethyl ether.

The reactions just given are those used in the commercial preparation of this compound. Ethyl ether is a very volatile and inflammable liquid, which boils at  $34.6^\circ$ . It is only slightly soluble in water, and water is still less soluble in it. It is an excellent solvent for fats, waxes, and many other organic substances which are insoluble in water, and large quantities of it are used in chemical laboratories for this purpose. It is also used as an anesthetic in surgery.

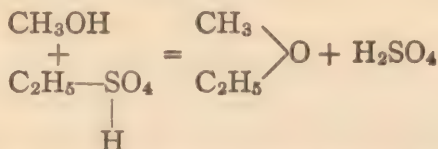
Although it resembles sodium oxide in structure, ethyl ether differs from that compound in being quite inactive chemically. However, when heated with water in the presence of a little acid, which acts as a catalytic agent, a molecule of water is added to one of ether, and two molecules of alcohol are formed:



**Mixed Ethers.**—If, in the second reaction given above in the preparation of ethyl ether, methyl alcohol



had been used instead of ethyl alcohol, the reaction would have proceeded as follows:



A mixed oxide, or a mixed ether would have been formed.

The reactions given provide a method for the preparation of any ether from the corresponding alcohols. It is evident that the general formula for the

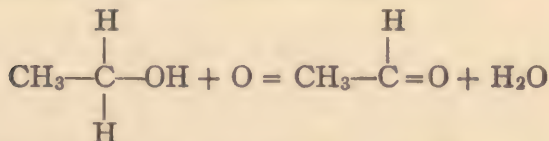
ethers is  $\begin{array}{c} \text{R} \\ \diagup \\ \text{R} \end{array} \text{O}$ , in which the two Rs may represent

the same, or different, alkyl radicals. The general method for the preparation of the ethers, and the general chemical reactions they undergo may be written by substituting R for the alkyl radicals in the above reactions.

## CHAPTER IV

### THE ALDEHYDES AND KETONES

**Acetaldehyde.**—This compound has been mentioned as the first stable product of the oxidation of ethyl alcohol. Leaving out the intermediate step, the equation for its formation is as follows:

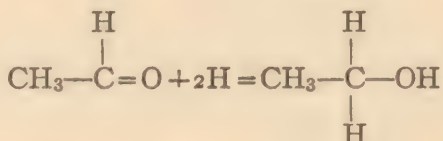


Acetaldehyde is a liquid boiling at  $21^\circ$ . It has a suffocating odor, resembling somewhat that of  $\text{SO}_2$ . It is used as a solvent for such substances as sulfur and phosphorus, and in the preparation of certain synthetic dyes.

**Addition Reactions.**—Acetaldehyde is much more active chemically than the compounds so far studied. A large part of this activity is due to the presence in its molecule of the divalent  $>\text{C}=\text{O}$  group, which is called carbonyl. The carbon and oxygen are united by two valences. A double bond uniting two atoms does not hold them together more firmly than a single bond, but rather less so. It also makes possible the formation of addition products, which is impossible

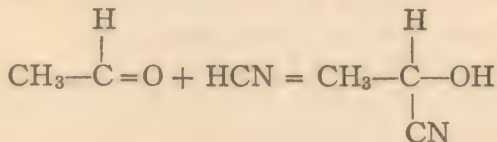
when atoms are united by single valences. The reactions which acetaldehyde undergoes may be divided into three groups. One of these includes reactions of addition. One of the bonds connecting the carbon with the oxygen may open, and a monovalent atom or group may be added to each end of it. Thus one of the atoms or groups will be combined with carbon, the other with oxygen.

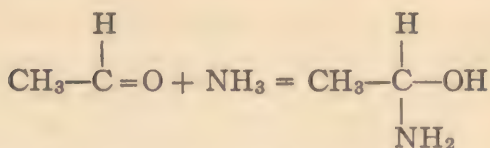
When acetaldehyde is treated with nascent hydrogen, such a reaction occurs, and ethyl alcohol is formed:



This is an addition reaction, and also a reduction reaction, since one of the valences of the carbon atom has been changed from positive to negative, and a positive atom has been added to both the carbon and the oxygen.

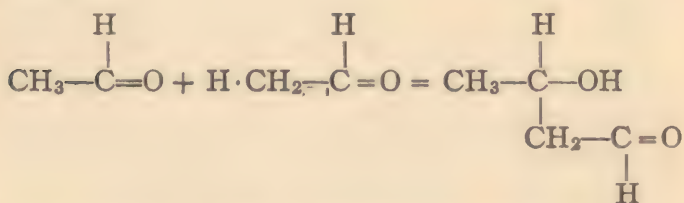
Acetaldehyde undergoes other addition reactions in which no changes in the state of oxidation occur. In such cases the positive atom or group combines with the oxygen atom, and the negative atom or group with the carbon atom. The following are examples of such reactions:





In these cases the aldehyde is saturated by the addition of the positive hydrogen to the oxygen atom, and of the negative groups  $-\text{CN}$  or  $-\text{NH}_2$  to the carbon atom. The organic cyanides are used frequently as intermediate steps in the synthesis of more complex organic compounds. The addition product with ammonia is a crystalline solid. As it is only slightly soluble, its formation may be used as a method for the purification of acetaldehyde. The aldehyde may be recovered from its ammonia addition product by warming with dilute acid.

A molecule of acetaldehyde also may be saturated by the addition of a second molecule of acetaldehyde. The reaction which occurs is shown in the following equation:

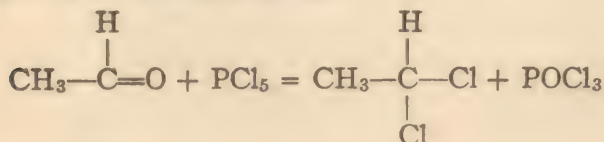


This reaction occurs in the presence of dilute alkali. As in the addition of hydrocyanic acid or ammonia, no change in the state of oxidation occurs. A positive hydrogen atom from the  $\text{CH}_3$ -group of the second molecule of acetaldehyde combines with the oxygen

atom of the first molecule, and the remaining monovalent negative group combines with the carbon atom to which that oxygen atom is united. The product formed in this reaction, aldol, contains an aldehyde group, and is similar in its chemical properties to acetaldehyde. Such a reaction, in which two or more molecules of a compound unite to form a more complex compound, is called polymerization. Thus acetaldehyde polymerizes to form aldol, and aldol is a polymer of acetaldehyde.

Other polymers of acetaldehyde are known. Three molecules may combine to form a pleasant smelling liquid with none of the properties of an aldehyde. This is called paraldehyde, and it is sometimes used in medicine as a sleep producer. Under slightly different conditions, three molecules of acetaldehyde combine to form a crystalline solid called metaldehyde. When treated with strong alkali, still higher polymers of acetaldehyde of unknown molecular weight are formed. These are called aldehyde resins.

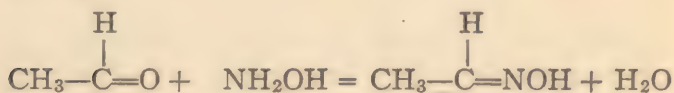
**Substitution Reactions.**—In a second group of reactions of acetaldehyde, the oxygen of the aldehyde group is replaced by two monovalent or by one divalent atom or group. These may be called substitution reactions. When acetaldehyde is treated with phosphorus pentachloride, two atoms of chlorine replace the oxygen of the aldehyde group:



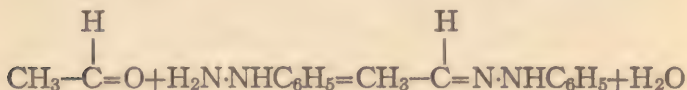


It will be noticed that no hydrochloric acid is liberated in this reaction. The liberation of hydrochloric acid on treating an organic compound with phosphorus pentachloride indicates the presence of an hydroxyl group in the molecule. This occurs, for instance, with the alcohols. When only carbonyl oxygen is present, a reaction occurs as is indicated above, but no hydrochloric acid is formed.

Two substitution reactions with nitrogen containing compounds are used in the purification and identification of aldehydes. With hydroxylamine an oxime is formed:



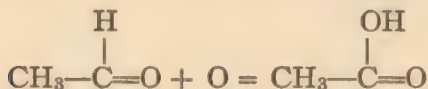
With phenylhydrazine a hydrazone is produced:



These reactions are especially valuable in the study of the sugars.

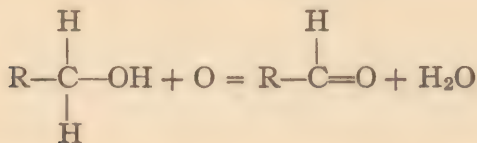
**Oxidation.**—One of the most characteristic and important properties of acetaldehyde is the ease with which it is oxidized. In other words it is a very good reducing agent. Alkaline solutions of certain metals are reduced by it very rapidly. Ammoniacal silver nitrate, when treated with acetaldehyde, is reduced, and metallic silver is deposited. If a solution of copper sulfate is made alkaline and heated with acetalde-

hyde, the copper is reduced to the cuprous condition, and cuprous oxide,  $\text{Cu}_2\text{O}$ , is precipitated. In these reactions the aldehyde is oxidized. As in the oxidation of the alcohols, the first step is the introduction of oxygen between carbon and hydrogen:



In this case the first product formed is stable, and, except in the presence of very strong oxidizing agents, the reaction goes no farther. The product, whose formula is given above, is acetic acid.

**The Aldehyde Series.**—Acetaldehyde is one of an homologous series of aldehydes, each of which is derived from the corresponding primary alcohol by oxidation. The general method for their preparation is given in the following equation:

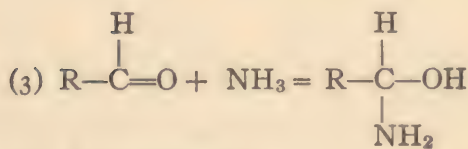
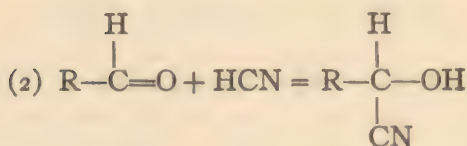
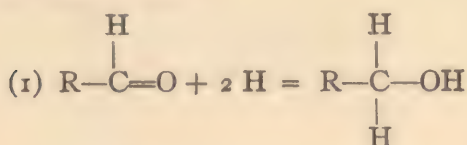


The lower members of the series, except the first, are liquids whose boiling points rise with increase in molecular weight. The higher members are solids whose melting points rise as the size of the molecule increases.

The chemical properties of all the aldehydes are the same as those that have just been given for acetalde-

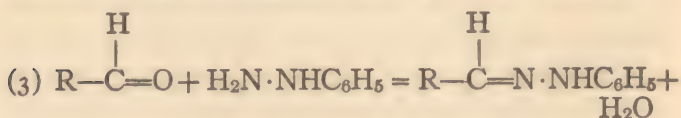
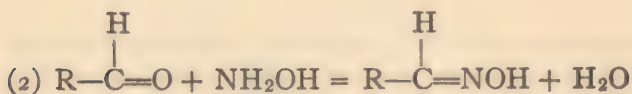
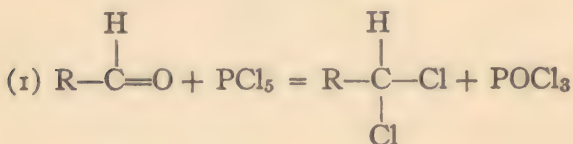
hyde. The equations are repeated below in their more general form:

### I. Addition reactions

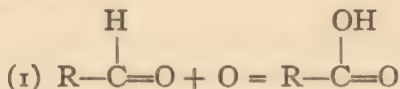


### (4) Polymerization

### II. Substitution reactions

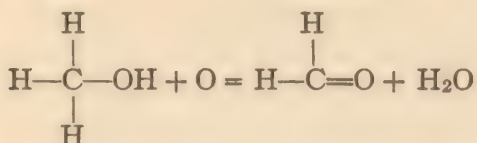


## III. Oxidation



The oxidation of any aldehyde yields the corresponding organic acid.

**Formaldehyde.**—The aldehyde formed by the oxidation of methyl alcohol is the first member of this series:



This product, formaldehyde, is a gas which liquefies at  $-21^\circ$ , and has a very pungent odor. It is soluble in water and is usually sold as a 40 per cent solution under the name Formalin. It is prepared commercially in large amounts by the oxidation of methyl alcohol. A mixture of air and methyl alcohol vapor is led over a heated spiral of copper or platinum wire. The oxidation begins at once, and liberates enough heat to keep the wire at the required temperature.

Formaldehyde is an excellent disinfectant. Immense quantities of it are used to destroy the spores of plant diseases on seeds of the grains, and on potato tubers. It is also used extensively to fumigate rooms to destroy pathogenic bacteria. For this purpose, the gas is driven from formalin by heating in the tightly closed room. The liquid may be heated by a flame of

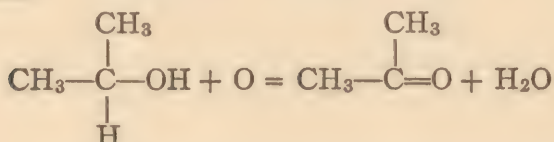
some kind, but on account of the danger of fire it is safer to pour the formalin into some oxidizing agent. Potassium permanganate or bleaching powder may be used. The oxidation of part of the formaldehyde liberates enough heat to vaporize most of the remainder.

Formaldehyde is a good preservative, and it is used for keeping such material as anatomical specimens. Several organic substances are hardened when treated with formaldehyde. The gelatin used on photographic films may be hardened in this way. Casein, a protein found in milk, when hardened by formaldehyde is used as a substitute for ivory in the manufacture of such articles as billiard balls. Certain complex phenols, hardened in the same way, make excellent substitutes for amber and for hard rubber.

It will be noticed that the molecule of formaldehyde contains no alkyl radical. In this respect it differs from all the other members of the series. It differs from the other aldehydes also in some of its chemical properties, although in most of its properties it is the same as acetaldehyde. It does not form an addition product with ammonia, and it is oxidized much more easily than the other aldehydes. One of its polymers is "Paraform," a white solid, which is decomposed into formaldehyde on heating. It does not form resins when treated with alkalies, but, under proper conditions, it forms a polymer having the formula  $C_6H_{12}O_6$ . This compound resembles the natural sugars very closely. It is possible that sugars are formed in the leaves of plants by a similar polymerization of formaldehyde.



**Ketones.**—Just as aldehydes are formed by the oxidation of primary alcohols, ketones are formed by the oxidation of secondary alcohols. This is illustrated in the following equation for the oxidation of isopropyl alcohol:



The product formed in this case is acetone. It is one of the products of the destructive distillation of wood, and it is prepared commercially from this source. It is also formed, along with butyl alcohol, by the action of certain bacteria on sugars. Some acetone is often present in the urine, and, in certain diseases, its amount is increased very greatly.

Acetone is a colorless, volatile, inflammable liquid which is miscible with water in all proportions. It is an excellent solvent for many organic substances, and is used in this way in the manufacture of such products as celluloid and explosives. It is also used as a reagent in the manufacture of iodoform, chloroform, and many synthetic drugs. It dissolves acetylene readily, and is used in the tanks in which this gas is stored.

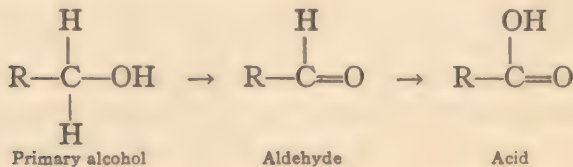
The molecule of acetone resembles that of acetaldehyde in containing a carbonyl group, but differs from the aldehyde in having an alkyl radical in place of the hydrogen of the aldehyde group. In most of its chemical properties, acetone resembles acetaldehyde quite

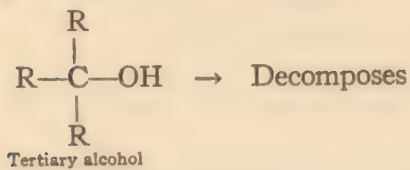
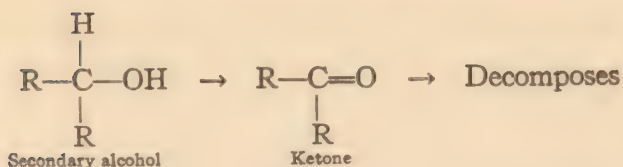
closely. An important difference is the product of its oxidation. As there is no hydrogen atom attached to the carbon atom of the carbonyl group, it is not possible for oxidation to yield an acid having the same number of carbon atoms as acetone. The ketone is much less easily oxidized than is the aldehyde, and when oxidized it is decomposed into two or more parts, containing fewer carbon atoms than the original ketone.

Since the ketones are produced by the oxidation of secondary alcohols, their general formula is  $\text{R}-\overset{\text{R}}{\underset{|}{\text{C}}}=\text{O}$ ,

in which the two alkyl radicals may be the same or different. It is evident that a very large number of different ketones is possible. With the exception of certain of the sugars which will be mentioned later, acetone is the only one of the ketones of enough practical importance to warrant discussion here.

In a previous chapter, primary, secondary, and tertiary alcohols were distinguished on the basis of the products of their oxidation. It is possible now to carry this distinction further. This is done in the following outline, in which no attempt is made to balance the reactions, but only the products of the oxidations are indicated:

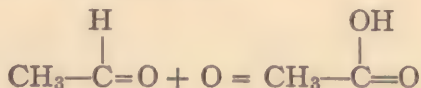




## CHAPTER V

### THE ACIDS AND ACID CHLORIDES

**Acetic Acid.**—The first product of the oxidation of acetaldehyde is acetic acid:



It is a weak acid, only slightly dissociated in solution. It forms salts with the metals, and in these salts the metal takes the place of the hydrogen of the hydroxyl group. The hydroxyl group of acetic acid is, then, quite different from that of the alcohols. It is not at all basic, but distinctly acid in character. Similar differences in the nature of hydroxyl groups are met in inorganic compounds. Thus the structural formula

for nitric acid is  $\text{HO}-\text{N} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array}$ , and that for sulfuric

acid  $\begin{array}{c} \text{HO} \\ \diagdown \\ \text{S} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array} \\ \diagup \\ \text{HO} \end{array}$ . The acid hydrogen in each of these

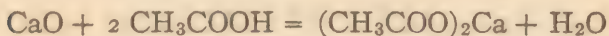
compounds is part of an hydroxyl group. Acids and bases differ in the point at which dissociation occurs. In acids this is between the hydrogen and the oxygen

of the hydroxyl group. In bases it is between the oxygen and the metal to which it is joined. Mention has been made of such compounds as zinc hydroxide which may dissociate in either way, depending on the conditions to which it is subjected. Such compounds are called amphoteric electrolytes.

When pure, acetic acid is a crystalline solid, melting at  $16.7^{\circ}$ . It resembles ice so strikingly that the pure acid is called glacial acetic acid.

As ordinarily prepared, acetic acid is a liquid which boils at  $119^{\circ}$ . It mixes with water in all proportions, and it is difficult to remove the last traces of water from the acid. It has a sharp sour taste and a penetrating smell. The concentrated acid blisters the skin.

**Preparation and Uses.**—Together with methyl alcohol and acetone, acetic acid is a product of the destructive distillation of wood. The aqueous layer of the distillate is treated with lime, and the calcium salt of acetic acid is formed:



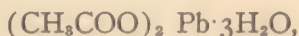
The methyl alcohol and acetone are distilled off, the remaining solution is evaporated, and solid calcium acetate crystallizes. This salt is treated with an acid, such as hydrochloric or sulfuric, and the acetic acid which is liberated is purified by distillation.

There are certain bacteria that are able to oxidize ethyl alcohol to acetic acid, probably forming acetaldehyde as an intermediate product. It is by the action of these bacteria that fermented fruit juices are changed into vinegar. The formation of vinegar from cider,



or other fruit juices, in barrels, is a rather slow process because the necessary oxygen from the air cannot penetrate the liquid rapidly. The change is brought about much more rapidly if the dilute alcoholic juice is made to trickle over beech shavings that have been inoculated with the acetic acid bacteria. Plenty of air can be supplied to furnish the oxygen needed, and the formation of acetic acid goes on very rapidly.

Acetic acid is useful in the laboratory as a solvent and reagent, and it is used in the manufacture of white lead and coal-tar dyes. Many of its salts are used extensively. Lead acetate,



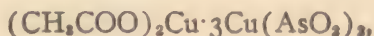
also called sugar of lead, is used as a laboratory reagent and also as a medicine. Solutions in which sugars are to be determined are often clarified by the addition of basic lead acetate,



Verdigris, a basic copper acetate,



is a green pigment, and Paris green, a mixed copper salt of acetic and metarsenous acids,

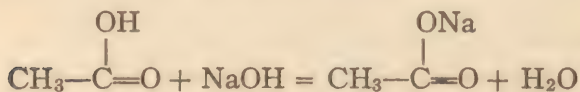


is a pigment and an insecticide. The acetates of aluminum, chromium, and ferric iron are used as

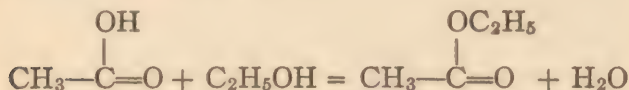
mordants in dyeing. When solutions of these salts are heated, basic acetates are precipitated. This property is made use of in the quantitative determination of these metals.

**Chemical Properties.**—In chemical properties, acetic acid differs from the aldehydes in being comparatively stable. The reactions it undergoes are mostly due to the hydroxyl part of the acid, or carboxyl group.

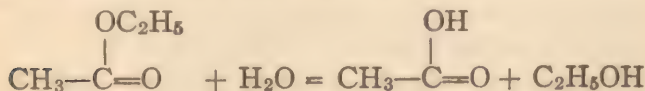
It reacts with bases to form salts:



Alcohols react with it in a way somewhat resembling the equation just given:



The product formed is ethyl acetate, a saltlike compound in which the ethyl radical takes the place of the metal of a salt. Such compounds are called esters. The nature of the action of an alcohol on an acid has been discussed (see Methyl Alcohol). The alcohols are but very slightly dissociated, and they react with acids slowly. Besides this, water and ethyl acetate react to form ethyl alcohol and acetic acid:

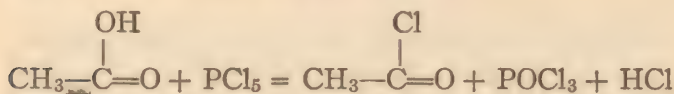


In other words, the reaction for the formation of an ester is reversible, and goes in both directions at the same time. The rate at which the reaction proceeds in either direction depends on the concentration of the reacting substances. When pure ethyl alcohol and acetic acid are mixed, the formation of ethyl acetate and water goes quite rapidly, but it goes more and more slowly as the alcohol and acid are used up, and their concentration is lessened. On the other hand, the formation of acid and alcohol from ester and water goes very slowly at first because only small amounts of these compounds are present. The rate of the reaction in this direction increases as more ester and water are formed. In the first of the above equations, the rate to the right is decreasing and that to the left is increasing, due to changes in the concentration of the reacting substances. It is evident that, in time, a point will be reached at which the rates in the two directions will be the same; no further changes in the concentrations of the reacting substances will occur; and the reaction will appear to have come to a stop. The point of equilibrium has been reached.

It is possible to change the point of equilibrium by changing the concentration of one of the reacting substances. Thus, if more water is added, some of the ester will be decomposed and more acid and alcohol formed. If water is removed, more ester will be formed. If the water can be removed as fast as it is formed, all the alcohol and acid will combine to form ester. This may be done practically by adding a dehydrating agent to the reaction mixture. Sulfuric

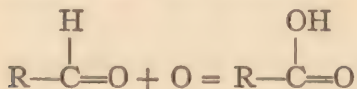
acid, which has a strong affinity for water, is often used.

Since acetic acid contains both an hydroxyl and a carbonyl group, there are two ways in which phosphorus pentachloride might be expected to react with it. However, it reacts only with the hydroxyl group, just as it does with the alcohols:

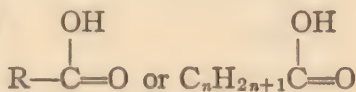


The resulting compound is acetyl chloride, one of a group of compounds called acid chlorides. Their properties will be discussed at the end of this chapter.

**The Fatty Acid Series.**—Acetic acid is a member of an homologous series of acids, each of which may be prepared from the corresponding member of the aldehyde series by oxidation. The general method for the preparation of these acids is:



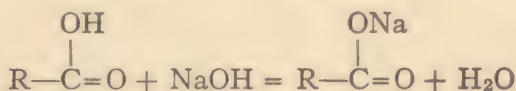
Their general formula is



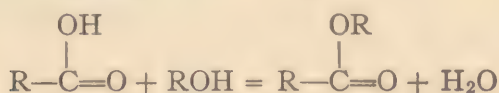
The physical properties of the acids vary with changes in molecular weight, just as do those of the other series studied. The lower members are volatile liquids; the higher members are less volatile; and those with still higher molecular weight are waxlike solids.

Many of the acids of this series occur naturally, especially combined with glycerol in the fats. Because of this, the series is called the fatty acid series. A compound of butyric acid,  $C_3H_7COOH$ , with glycerol occurs in butter fat to the extent of about 6 per cent. Palmitic acid,  $C_{15}H_{31}COOH$ , and stearic acid,  $C_{17}H_{35}COOH$ , are the ones which occur most abundantly in all the fats.

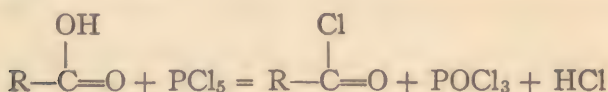
**Chemical Properties.**—In general the chemical properties of all of the series are the same as those that have been given for acetic acid. They react with bases to form salts:



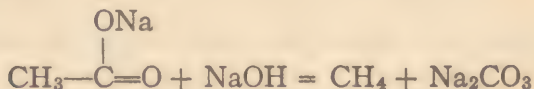
and with alcohols to form esters:



Phosphorus pentachloride reacts with the acids to form acid chlorides:

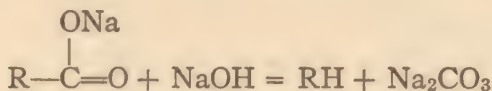


One of the methods given for the preparation of methane was the heating of sodium acetate with  $\text{NaOH}$ :

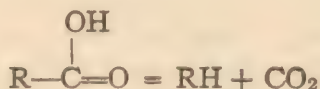




The same kind of a reaction occurs when the sodium salt of any of the acids of this series is heated with NaOH:

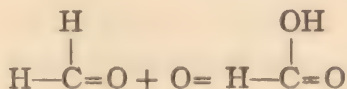


Sodium carbonate, and an hydrocarbon containing one less carbon atom than the acid, are formed. This is a convenient method which is often used in the laboratory for the preparation of pure hydrocarbons. If the details of the method are omitted, it will be seen that the reaction consists essentially of the removal of carbon dioxide from an acid:

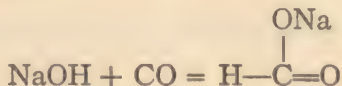


Although living organisms are not alkaline enough to carry out this reaction as it is done in the laboratory, in many cases they are able by other means to remove  $\text{CO}_2$  from organic acids. This will be mentioned again when the action of bacteria in the intestine is discussed.

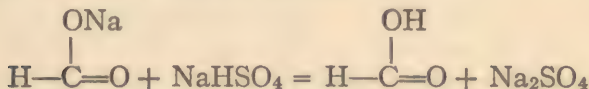
**Formic Acid.**—The first member of the fatty acid series is formed by the oxidation of formaldehyde:



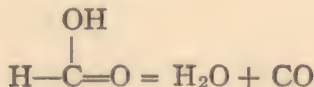
This is formic acid, which occurs in nettles and in ants, and to which their sting is due, at least in part. Its sodium salt is prepared commercially by heating sodium hydroxide and carbon monoxide together under pressure:



The acid may be liberated from its salt by distilling with sodium hydrogen sulfate:

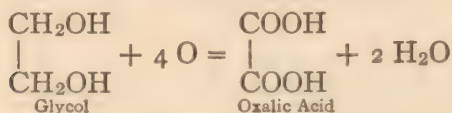


By this method, which has been developed rather recently, formic acid may be prepared so cheaply that it is replacing other organic acids that are used in dyeing and tanning. Formic acid is a colorless liquid which boils at  $101^\circ$ . It has a very sharp, pungent odor, somewhat like  $\text{SO}_2$ . The structural formula for formic acid shows that it is an aldehyde as well as an acid. For this reason its properties are different from those of the other acids of the series. It reduces alkaline solutions of the heavy metals, just as the aldehydes do, and is oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Although formic acid may be distilled without decomposition, if it is heated with a dehydrating agent it is decomposed into water and carbon monoxide:



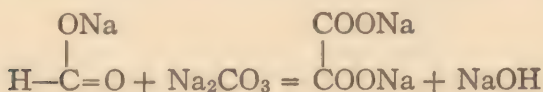
Sulfuric acid may be used as the dehydrating agent. This reaction furnishes an excellent laboratory method for the preparation of carbon monoxide.

**Dibasic Acids.**—Several acids containing two carboxyl groups are known. The simplest of these is oxalic acid, which may be formed by the oxidation of the dihydric alcohol glycol. Several intermediate compounds are formed, but the net result of the oxidation is shown in the following equation:



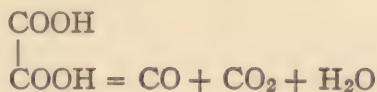
Glycol contains two primary alcohol groups, each of which is oxidized to carboxyl.

Oxalic acid may be prepared by oxidizing sugars with nitric acid. Its sodium salt is prepared commercially by heating cellulose (sawdust) with sodium hydroxide; also by heating sodium formate with sodium carbonate:



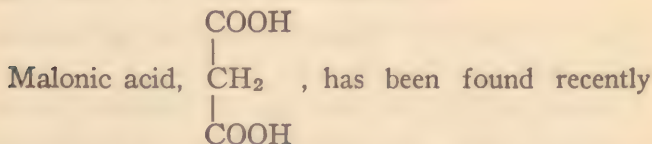
Oxalic acid is a colorless crystalline solid, which is quite soluble in water. On heating, it decomposes into carbon dioxide and formic acid. If heated with a dehydrating agent, the formic acid is further decomposed into carbon monoxide and water. Thus on heat-

ing oxalic acid with concentrated sulfuric acid, the following changes occur:

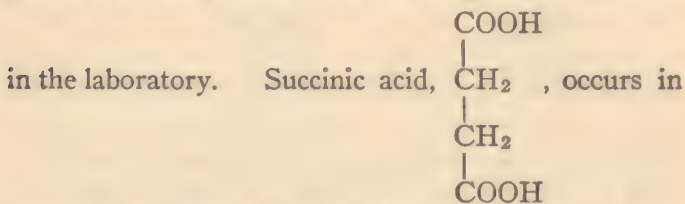


The potassium and calcium salts of oxalic acid are widely distributed in plants; the latter, which is insoluble, in the form of crystals. This is also the form in which calcium is usually precipitated in analytical work. The potassium hydrogen salt,  $\text{COOK}$ , is

largely used in dyeing and in the manufacture of cleaning compounds, bleaches, and polishes.



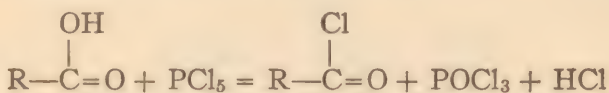
among the products of the action of certain microorganisms on sugars. It occurs very rarely in nature, but it is one of the most important intermediate compounds in the synthesis of other organic compounds



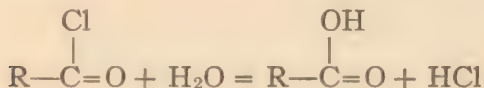
amber, in fossilized wood, and in many plants.

**The Acid Chlorides.**—The acid chlorides do not occur in nature, but, because of their great chemical

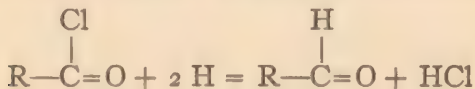
activity, they are very useful in the synthesis of many compounds in the laboratory. They are used in this way in place of the much less active acids from which they are derived. They may be prepared by treating acids with phosphorus pentachloride:



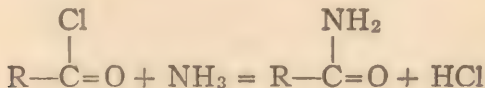
They must be kept dry, since they react very readily with water to reform the acids from which they were prepared:



The acids cannot be reduced to aldehydes by hydrogen, but this reaction occurs with the acid chlorides:



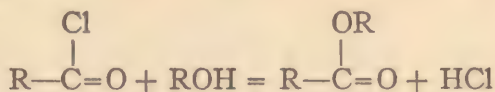
The acid chlorides react with ammonia in much the same way as do the monochlorine substitution products of the hydrocarbons. One of the hydrogen atoms of the ammonia combines with the chlorine of the acid chloride to form hydrochloric acid, and the remaining  $\text{—NH}_2$  group takes the place of the chlorine atom thus removed:





The products of such reactions are acid amides, one of the most important of the groups of nitrogen-containing compounds. Along with the cyanides and amines, they will be discussed later.

Esters are formed by the action of alcohols on acid chlorides:



This reaction is often used in the laboratory, as it goes much more readily than the direct action of an alcohol on an acid.

## CHAPTER VI

### ESTERS AND FATS

Esters are formed from alcohols by replacing the hydroxyl group by an acid radical. The acid may be either inorganic or organic. The monochlorine substitution products of the paraffin hydrocarbons and the trinitrate of glycerol are examples of esters of inorganic acids. In this chapter only esters of organic acids will be considered.

**Preparation.**—Esters may be prepared by the direct action of an acid on an alcohol:



As has been stated, this reaction does not go to completion unless some means are provided to remove one of its products. Thus, in the presence of a strong dehydrating agent, such as concentrated sulfuric acid, a large proportion of the total amount of ester possible may be obtained, because of the removal of the water which is formed at the same time. This method is undoubtedly used in a very great many syntheses that are carried out by living organisms, but the method by which they are made to go even approximately to completion is not known. Esters may also

be prepared by the action of an alcohol on an acid chloride:



Small amounts of esters may be prepared very conveniently by treating the monochlorine substitution product of a hydrocarbon with the silver salt of an acid:



**Occurrence.**—The esters of acids with monohydric alcohols are quite widely distributed in nature, though they do not usually occur in very large amounts. Those of the lower acids and alcohols are volatile substances, only slightly soluble in water, but readily dissolved by organic solvents such as ether and chloroform. They have pleasant fruity odors, in fact they are the substances which give many fruits their characteristic flavors. The following are examples of some of the flavors possessed by certain of the esters:

Ethyl butyrate	$\text{C}_3\text{H}_7\text{COOC}_2\text{H}_5$	Pineapple
Amyl acetate	$\text{CH}_3\text{COOC}_5\text{H}_{11}$	Pear
Octyl acetate	$\text{CH}_3\text{COOC}_8\text{H}_{17}$	Orange
Amyl butyrate	$\text{C}_3\text{H}_7\text{COOC}_5\text{H}_{11}$	Apricot

Since the alcohol and acid radical may be the same or different, it is evident that a great variety of esters is possible. By the use of a suitable mixture of esters, the flavor of almost any fruit may be imitated.

The esters of acids and alcohols of higher molecular weight are called waxes. A few of them are liquids,

but most of them are solids, resembling the fats in physical properties. They are insoluble in water, but soluble in organic solvents. The names and occurrence of a few of them are listed below:

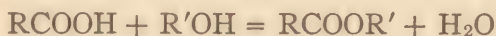
Myricyl palmitate,  $C_{15}H_{31}COOC_{30}H_{61}$ ,  
occurs in beeswax.

Cetyl palmitate,  $C_{15}H_{31}COOC_{16}H_{33}$ ,  
occurs in spermaceti.

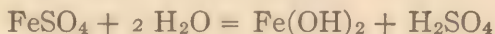
Ceryl myristate,  $C_{13}H_{27}COOC_{26}H_{53}$ ,  
occurs in wool wax.

Esters of certain acids with the trihydric alcohol glycerol are fats. Because of their importance these will be discussed separately.

**Hydrolysis and Saponification.**—The formation of esters by the interaction of acids and alcohols is called esterification:



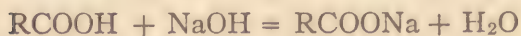
This reaction does not go to completion, but is reversible; proceeding to the left it is called hydrolysis. In inorganic chemistry, hydrolysis is sometimes defined as the action of water on a salt to form an acid and a base, one of which is but slightly dissociated. Thus ferrous sulfate in solution is acted on by water and part of it is changed as follows:



Ferrous sulfate is but slightly dissociated and the solution is acid in reaction due to the formation of the strong sulfuric acid. The action of water on an ester

to form an alcohol and an acid is very similar to this, except that both products are only very slightly dissociated. Many other organic compounds are decomposed by water, but alcohols and acids are not always formed. Such reactions will be met frequently, as they are especially common in living organisms. They are properly called hydrolyses, but in order to include them the definition must be made more general. In the sense in which it is used here, hydrolysis is the decomposition of a molecule into two or more parts with the addition of the elements of water.

The hydrolysis of an ester, like its formation, is not complete unless some means are taken to remove one of the products formed. This may be done, practically, by adding an alkali to neutralize the acid as it is formed. Although this does not remove the acid from solution, it changes its form so that practically none of it is left to react with the alcohol and reform the ester. The equations for the reactions may be written in steps as follows:



It is customary to combine the two equations as follows:



The net result, then, is that an alkali reacts with an ester to form an alcohol and the salt of an acid. This type of reaction is called saponification. The reason for this name will appear when the fats are studied.



**Review.**—The outline given on page 42 may now be extended to include several more reactions and

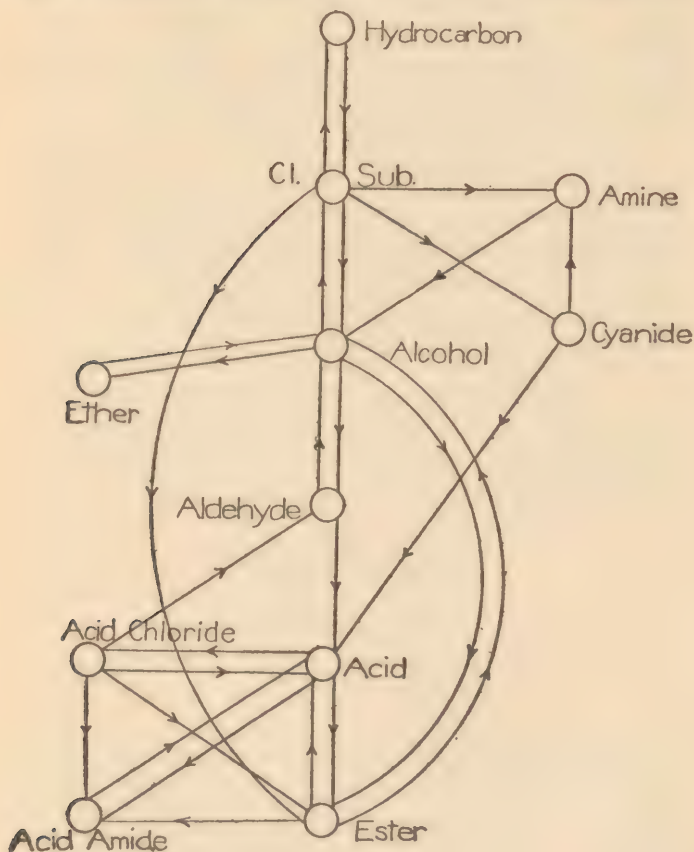
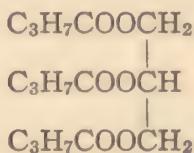


FIG. 5.

groups of compounds. A few groups not studied as yet have been added for future reference. All the groups of compounds listed are related to each other,

and starting with any one it is possible, by using the methods indicated, to prepare the corresponding member of any other group. Remembering the note given under the outline on page 42, it would be excellent practice to write equations for the reactions by which ethyl acetate might be prepared from methane.

**The Fats: Definition.**—The fats are naturally occurring esters of certain organic acids with the trihydric alcohol glycerol. As there are three alcoholic hydroxyl groups in the molecule of glycerol, three molecules of a monobasic acid may combine with it. The fats are compounds in which all three of the hydroxyl groups of glycerol have been esterified by certain monobasic organic acids. The chemical structure of the fats is illustrated by the following formula for butyrin, in which butyric acid has formed esters with the three hydroxyl groups of glycerol:



**Occurrence.**—The fats are one of the three groups of food substances, and are found in varying amounts in all living cells. Much larger amounts occur as storage material in plants and animals. In plants they are most abundant in the seeds of certain species, where they serve as a reserve supply of food which helps to support the young plant until it has developed sufficiently to be able to manufacture its own

food. In animal bodies fat is stored around the internal organs and in a layer under the skin. Fat is the principal form in which food is stored in animals. It forms a reserve supply which may be used during unusual exertion, or when the diet is insufficient. The principal function of fats in the body is to furnish energy, which is liberated by the oxidation of the fat. Under normal conditions the oxidation is complete and the only products formed are carbon dioxide and water. The fats are very stable substances chemically, and in order to oxidize them in the laboratory, very powerful oxidizing agents are required. In some way living cells are able to bring about this oxidation quite easily.

Fats are extracted from animal or plant tissues on a commercial scale by several methods, depending on the nature of the tissue and the uses to which the fat is to be put. Vegetable oils of the best quality are obtained by crushing the seeds in which they occur, and subjecting the mass to high pressure. A better yield of a somewhat poorer quality of oil may be obtained by heating and pressing. By the use of fat solvents, such as ether, chloroform, benzine, or carbon bisulfide, the oil may be removed completely, but it is difficult to remove the last traces of the solvent from the fat, and oils prepared in this way are not as satisfactory for foods as those obtained by cold pressing. Animal fats are usually separated from the tissue in which they occur by heating. Immense amounts of fats in the form of butter, lard, and various oils are used as food. Fats are also the most important raw

materials in the manufacture of soap, glycerin, and paints.

The naturally occurring fats are not pure compounds, but are composed of mixtures of esters of glycerol with several organic acids. In general, however, a given species produces a fat that is quite uniform in composition, and characteristic of the species. Thus the properties of a fat may be used in determining the source from which it was obtained. The name of a pure fat is derived from that of the acid with which glycerol is combined. Thus the ester of glycerol with butyric acid is called butyrin; that with stearic acid, stearin; and that with oleic acid, olein.

**The Acids Occurring in Fats.**—Since glycerol is common to all the fats, the differences among them must be due to differences in the acids with which the glycerol is combined. The series of acids of which acetic acid is a member is called the fatty acid series, because many of its members occur in the fats. The following members of this series have been found combined with glycerol in the fats:

Acetic	$\text{CH}_3\text{COOH}$	Myristic	$\text{C}_{13}\text{H}_{27}\text{COOH}$
Butyric	$\text{C}_3\text{H}_7\text{COOH}$	Palmitic	$\text{C}_{15}\text{H}_{31}\text{COOH}$
Caproic	$\text{C}_5\text{H}_{11}\text{COOH}$	Stearic	$\text{C}_{17}\text{H}_{35}\text{COOH}$
Caprylic	$\text{C}_7\text{H}_{15}\text{COOH}$	Arachidic	$\text{C}_{19}\text{H}_{39}\text{COOH}$
Capric	$\text{C}_9\text{H}_{19}\text{COOH}$	Behenic	$\text{C}_{21}\text{H}_{43}\text{COOH}$
Lauric	$\text{C}_{11}\text{H}_{23}\text{COOH}$	Lignoceric	$\text{C}_{23}\text{H}_{47}\text{COOH}$

Of these, palmitic and stearic acids occur most commonly and in largest amounts. Butter fat contains about 6 per cent of butyrin. The first few members of this series are liquids whose boiling points rise with increased molecular weight. The higher members are solids whose melting points rise as the molecular weight increases. This difference is also apparent in the fats in which these acids are combined. Thus a fat composed largely of stearin is hard, but one composed largely of the esters of the lower fatty acids with glycerol is soft or even liquid.

A few other acids than those mentioned also occur in the fats. The most important of these contain the same number of carbon atoms as stearic acid, but fewer hydrogen atoms. They do not, then, correspond to the general formula which has been given for the acids of the acetic series,  $C_nH_{2n+1}COOH$ . Following are the names and formulas of the three most important of these acids:

Oleic             $C_{17}H_{33}COOH$

Linoleic        $C_{17}H_{31}COOH$

Linolenic       $C_{17}H_{29}COOH$

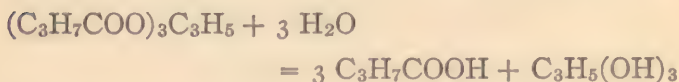
They are present in large amounts in many vegetable fats, such as linseed oil, cottonseed oil, and olive oil. Although these acids have high molecular weights, they are liquids, and the fats in which their glycerol esters occur in large amounts are also liquids.

**Physical Properties.**—The fats are insoluble in water but soluble in many organic solvents, such as



ether, petroleum ether, chloroform, and alcohol. Many fats are liquids at ordinary temperature. This is especially true of those that contain large amounts of the esters of the unsaturated acids mentioned at the end of the preceding paragraph. Such fats are called oils. In this sense, oils are fats that are liquids at ordinary temperatures. In general the term "oil" has no very definite meaning, since it is also applied to the liquid hydrocarbons, to the volatile substances which give flavor to fruits and odor to flowers, and to many other substances which are not at all related to the fats chemically. The fats are not volatile. They are lighter than water, varying in specific gravity from 0.915 to 0.970.

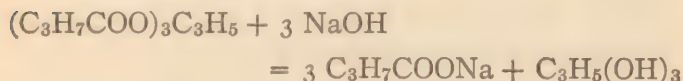
**Chemical Properties: Hydrolysis.**—Chemically the fats are rather inert substances. Aside from the oxidation which they undergo in living cells, their most important reaction is that of hydrolysis. The hydrolysis of butyrin is illustrated in the following equation:



This reaction goes very slowly indeed, perhaps because of the insolubility of fats in water. By the use of an appropriate catalyst, it may be made to go quite rapidly, though it does not go to completion. A complex organic compound of sulfuric acid is sometimes used to catalyze this reaction. The products are organic acids which are used for making soaps and candles, and glycerol from which nitroglycerin is made.

This hydrolysis and its reverse, the formation of fats from organic acids and glycerol, both may proceed rapidly in living cells. The catalyst which hastens the reaction in this case is an organic substance, secreted by the cell, called lipase.

**Saponification.**—As was mentioned under the esters, the hydrolysis of an ester may be made to go to completion by the addition of an alkali to neutralize the acid as it is formed. The reaction that occurs with butyrin is shown in the equation:

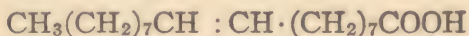


The salts of the higher acids occurring in fats are called soaps. It is for this reason that the reaction has been given the name saponification. The original meaning of the term was the action of an alkali on a fat to form a soap and glycerol. Because of the similarity of the action of alkalies on other esters, the term has come to be applied more generally. Saponification may be defined as the action of an alkali on an ester to form an alcohol and a salt of an acid. Both the glycerol and the alkali salt of the fatty acids formed by the saponification of fats, are soluble in water. The soaps, however, are insoluble in a moderately concentrated solution of NaCl, in which glycerol is soluble. After saponification, then, the soaps are separated by adding NaCl. They are lighter than the solution, so they rise, and are skimmed from the surface.

**Properties of the Soaps.**—If a fat, which is insoluble in water, is shaken with a soap solution, the fat is broken into minute drops which remain suspended in the solution. The soap appears to form thin layers around the droplets of fat, which keep them from running together. Such a suspension is called an emulsion, and the substance, soap in this case, which holds the fat in suspension is called an emulsifying agent. The cleansing power of soap is largely due to its ability to emulsify fats and other substances that are insoluble in water.

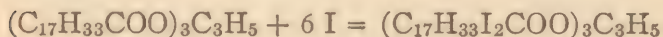
Water is said to be hard when it contains salts of calcium and magnesium. When soap is added to such water, insoluble calcium and magnesium soaps are formed, and no soap remains in solution until all these salts have been precipitated. As far as its cleansing effect is concerned, the soap precipitated by calcium and magnesium is wasted.

**The Iodine Number of Fats.**—The unsaturated acids which occur in fats differ in structure from the saturated acids. This is shown by the following formula for oleic acid:



Two of the carbon atoms are united by a double bond. If one of the bonds connecting these two carbon atoms should open, and a monovalent atom or group combine with each of the carbon atoms, the compound would be saturated and no further addition could occur. The addition of certain elements to such compounds happens very easily. The halogens are added especially

readily. Linoleic acid contains two such double bonds; and linolenic acid, three. If a fat containing the esters of these unsaturated acids is treated with a solution of iodine, two atoms of iodine are added to each of the double bonds. For the fat olein, the reaction is as follows:



The amount of iodine absorbed by a fat depends on the amount of the esters of unsaturated acids present in the fat. The number of grams of iodine absorbed by 100 grams of a fat is called the iodine number of the fat. This is a value that is often determined in the laboratory examination of fats.

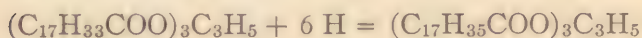
**Drying Oils.**—The double bonds in the unsaturated acids will add many other substances beside iodine. On exposure to the air they will take up oxygen. At the same time more or less polymerization occurs, and the oil hardens to a tough durable film. Oils that will harden, or “dry” in this way, are used in paints. Only oils that are very highly unsaturated will dry satisfactorily. From this standpoint, fatty oils are divided into three groups: (1) Drying Oils which are highly unsaturated and harden quickly. Linseed oil, which has an iodine number of about 180, is an example of this group. (2) Semi-drying Oils. These are less highly unsaturated than the drying oils. On exposure to the air, they absorb some oxygen and thicken but do not dry. Cottonseed oil, which has an iodine number of about 110, belongs to this group. These oils may be used to some extent



in paint, if they are mixed with drying oils. (3) Non-drying Oils. Though they may absorb some oxygen from the air, they do not even thicken. They are of no value for paints. Olive oil, iodine number about 80, is a member of this group.

The drying of oils may be hastened by the addition of catalysts. Lead oxide, lead oleate, and certain other metallic oxides and salts are used. They are incorporated with the oil by the process of boiling. Turpentine also acts as a catalyst in hastening the drying of oils. Drying oils are also used in the manufacture of oilcloth, linoleum, and printer's ink.

**Hydrogenation.**—Beside the halogens and oxygen, hydrogen also may be added to the double bonds of the unsaturated fats. This does not add as easily as the other elements mentioned, but, by the use of suitable catalysts, the hydrogenation may be carried out readily. The reaction in the case of olein is shown in the following equation:



The formula for the product is the same as that for stearin. It resembles stearin, too, in some of its properties. Thus, though olein is a liquid, the product of its hydrogenation is a solid. The fat has been hardened. Immense amounts of such oils as cotton-seed oil, after being hardened, or hydrogenated, are used as substitutes for lard and other more solid fats.

**The Lipoids.**—Many substances occurring in living organisms are quite similar to the fats in physical properties, especially in their solubilities. It is con-



venient to classify these substances in one group which may be called the lipoids, or fatlike substances. Many of these compounds bear no chemical relation at all to the fats, but are classed here only because of their similar physical properties. The lipoids may be divided into the following groups:

1. The fats
2. The waxes
3. The solid alcohols or sterols
4. The essential oils
5. The lecithins and related substances

The fats have been discussed, and a few words will now be given to each of the other groups.

**The Waxes.**—The waxes have been defined as esters of organic acids of high molecular weight with the higher monohydric alcohols, and some examples of them have been given. The waxes function less frequently than the fats as reserve food materials. Many of them form an outer protective covering on fruits, leaves, and other parts of plants. In general, they are much more resistant to hydrolysis and saponification than are the fats. In ordinary language, the term wax is usually applied to any fatlike substance that is quite hard, without reference to its chemical nature. Often this use of the term and the chemical one do not agree. Thus bayberry wax is chemically a fat, and wool fat is chemically a wax. Two important commercial waxes are carnauba wax, which is collected from the leaves of a species of palm;

and spermaceti, which is obtained from the head of the sperm whale.

**The Sterols.**—The sterols (solid alcohols) resemble the fats very closely in their physical properties, but as they are not esters they are not saponifiable. Some of them are higher members of the group to which methyl and ethyl alcohols belong, but the most important ones differ very radically from these in structure. They are derivatives of the terpenes, which are complex hydrocarbons whose atoms are arranged around the following nucleus:

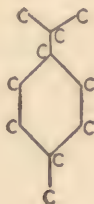


FIG. 6.

The most important and abundant member of this group in the animal kingdom is cholesterol,  $C_{27}H_{45}OH$ . It is a secondary alcohol, having one double bond, and containing four of the terpene nuclei just mentioned. It occurs in all the tissues of the body, but it is especially abundant in the brain and nervous tissue. In pathological conditions, it may form gallstones and deposits on the walls of the arteries. It has a powerful effect in preventing the action of certain poisons, like snake venom, which destroy the red blood corpuscles.

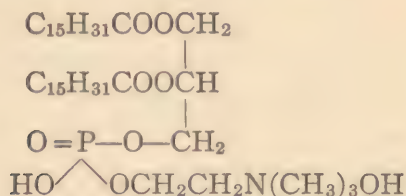
It has the property of taking up large amounts of water without going into solution.

An alcohol, or mixture of alcohols, called phytosterol, very similar in structure and properties to cholesterol, occurs in all vegetable fats. Cholesterol and phytosterol may be distinguished by the difference in the melting points of their esters with acetic acid. Since cholesterol occurs in all animal fats, and phytosterol in all vegetable fats, this difference in properties is sometimes of value in detecting adulterations. Many other similar alcohols are known, but none of them is of sufficient importance or of general enough occurrence to warrant discussion here.

**Essential Oils.**—The essential oils include a great number of compounds of quite widely different chemical structure. They are all volatile, and are the substances which give flavor and odor to fruits and flowers. Many of the best known members of this group belong to two classes of compounds: (1) Volatile Esters. Examples of these which have the flavors of various fruits have been given. (2) The Terpene Hydrocarbons and Their Derivatives. These are complex substances whose structure is built up around the nucleus given above. The hydrocarbons themselves do not have much fragrance, but many of the most highly prized perfumes are alcohols, aldehydes, ketones, or acids derived from these hydrocarbons. The extraction of these essential oils from flowers is a large industry in some localities, particularly in France. Two methods are employed principally in obtaining these essences; distillation of the flowers with steam, and a

process called enfleurage. In the latter process the flowers are placed between layers of some fat, such as lard, or of fairly solid paraffin hydrocarbons; the essences are dissolved as they escape from the flowers, and are recovered from the fat or paraffin by distillation with steam. This method gives a product of choicer quality than direct distillation, and also a larger yield, as the flowers continue to form the essential oil for some time after they have been layered.

**The Lecithins.**—The lecithins are quite similar to the fats in structure, except that they contain phosphoric acid and an organic nitrogen containing base, beside glycerol and fatty acids. Probably a great variety of lecithins exists, but the following formula may be considered typical of them:



The molecule is, then, composed of three parts: (1) part of a fat molecule; (2) phosphoric acid; (3) a nitrogen base, in this case choline. Lecithins occur in all living cells; like cholesterol, they have the property of imbibing a large amount of water without going into solution. Both are undoubtedly important in helping to maintain the peculiar semifluid consistency of protoplasm.

Similar substances containing sulfuric acid instead

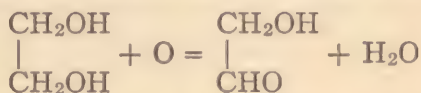
of phosphoric acid are known: they are called the sulfolipins. Others contain neither of the acids, but the nitrogen base, and are called the aminolipins. All of these occur especially abundantly in the brain and nervous tissue.



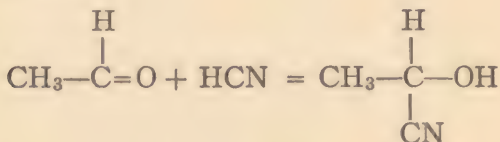
## CHAPTER VII

### MIXED COMPOUNDS

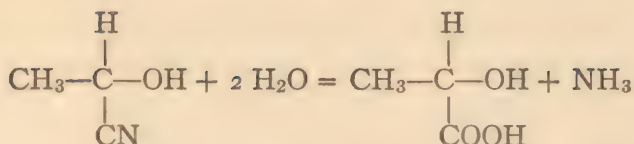
There are many compounds that belong to more than one of the groups that have been studied. The first step in the oxidation of the dihydric alcohol glycol to oxalic acid (page 73) yields such a compound:



This first product of the oxidation of glycol, glycol aldehyde, is both a primary alcohol and an aldehyde, and has the properties of both groups of compounds. The following synthesis will illustrate the formation of another such compound. Hydrocyanic acid will add to acetaldehyde, as has been stated in the chapter on the aldehydes:

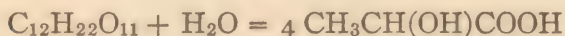


When a cyanide is heated with water in the presence of a little acid or alkali, it is hydrolyzed and an acid is formed:



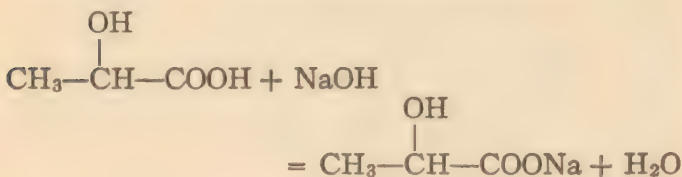
The compound formed in this case is lactic acid, which is both an acid and a secondary alcohol.

**Lactic Acid.**—Lactic acid is formed in milk by the action of bacteria on milk sugar:

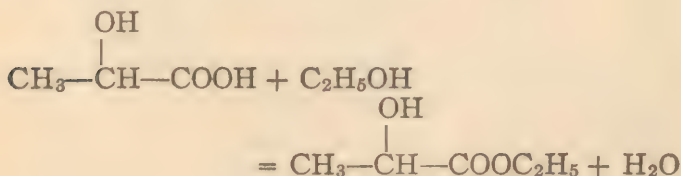


It is also the characteristic acid of corn silage and sauerkraut. It is formed in the muscles as an intermediate product in the oxidation of sugar. It is a thick, colorless, odorless liquid, with a specific gravity of 1.24. It absorbs water readily, and is soluble in water and alcohol.

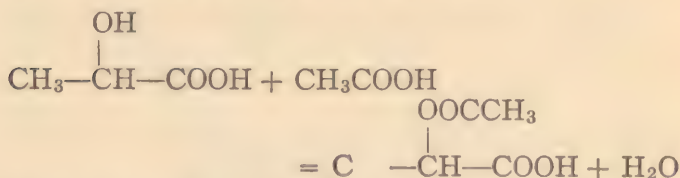
As an acid, lactic acid forms salts with bases:



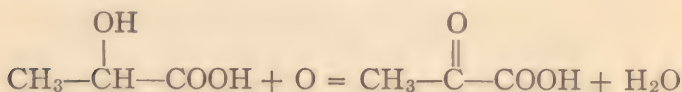
and esters with alcohols:



As an alcohol, it forms esters with acids:



Since it is a secondary alcohol, it yields a ketone on oxidation:



This ketone is pyruvic acid, which is probably another of the intermediate products in the oxidation of sugars in living cells.

**Isomerism of Lactic Acids.**—It is a peculiar fact that the lactic acid found in muscles is not the same as that obtained from sour milk. Their chemical properties and nearly all their physical properties are identical, but they differ in their effect on polarized light. Light which has been treated in such a way that all the vibrations, except those in a single plane, have been absorbed, is said to be polarized. If polarized light which is vibrating in a vertical plane is passed through a solution of the lactic acid obtained from muscles, it will emerge from the solution vibrating in a plane that is twisted to the right of vertical. If polarized light is passed through a solution of the lactic acid formed by certain bacteria, the plane of its vibration will be twisted to the left. Lactic acid is an optically active substance. One form of it rotates

the plane of polarized light to the right, and the other rotates it to the left to exactly the same extent. A mixture of equal parts of the two forms is without effect on the plane of polarization of light.

**Stereoisomerism.**—Many other organic compounds exist in two forms which have effects on polarized light similar to those of the two forms of lactic acid. It is found that in all cases such compounds contain at least one carbon atom which is combined with four different atoms or groups. Whenever a compound contains such a carbon atom, it exists in two forms which have the effect on polarized light that has been described. The four valences of the middle carbon atom of lactic acid are satisfied, respectively, by  $\text{CH}_3$ —, —OH, —H, and —COOH. Recalling the tetrahedral structure of carbon compounds which was discussed under methane, suppose this middle carbon atom of lactic acid to be in the center of the tetrahedron, and one of the four groups with which it is combined at each of the vertices. It will be found that there are two ways in which these groups can be arranged which are not identical. These two ways are illustrated in the figure below:

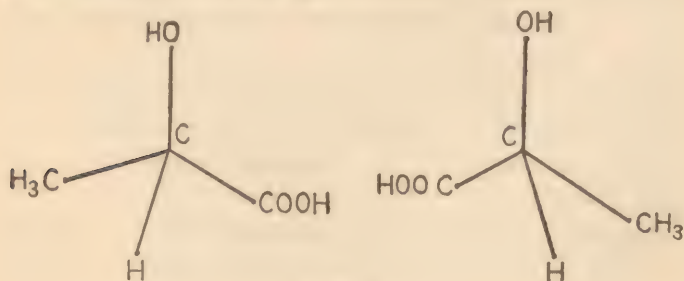
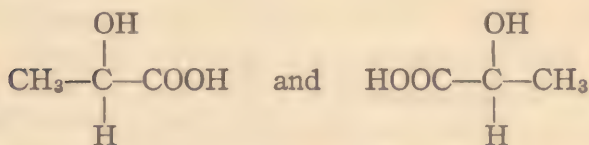


FIG. 7.

These two figures cannot be superposed, therefore they are not identical. They bear the same relation to each other that the right hand bears to the left, or that an object bears to its image in a mirror. This relation cannot be illustrated accurately on a plane surface, but the following structural formulas will serve to indicate it:



One of these formulas may be assumed to represent the form of lactic acid that rotates the plane of polarized light to the right, the other the one which rotates it to the left. Isomerism due to the two possible arrangements in space of four unlike atoms or groups around a carbon atom is called stereoisomerism, or space isomerism. A carbon atom combined with four different atoms or groups is said to be asymmetric.

The right, or dextrorotatory form of lactic acid is produced in muscles. It is also formed by the action of a bacterium, *Micrococcus acidi paralactici*, on sugars. Another bacterium, *Bacillus acidi laevolactici*, decomposes sugars with the formation of the left, or levorotatory form. Other bacteria produce equal parts of the two forms. Such a mixture is optically inactive.

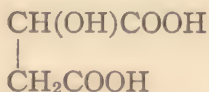
**Importance of Stereoisomerism.**—Whenever lactic acid is prepared in the laboratory, either by the



method given on page 97, or by any other method by which it may be synthesized, an inactive mixture of the two forms is produced. The same is true of the synthesis of any other compound containing an asymmetric carbon atom (one combined with four different atoms or groups). Although it has been tried very often, it has been impossible, so far, to synthesize one form of an asymmetric compound to the exclusion of the other, without the aid of living organisms. But when such compounds are formed by living organisms, it very often happens that one, and only one, of the two possible forms is produced. There are, also, specific differences in this regard. This is illustrated by the case of the two species of bacteria mentioned above. One of them produces the dextrorotatory form of lactic acid, the other the levorotatory form. Similar differences are observed in the use of such compounds by living organisms. Thus if the mold, *Penicillium glaucum*, is grown in a medium containing both of the forms of lactic acid, it uses the levo form and leaves the dextro form untouched. It is possible that there is something about the structure of the protoplasm of this mold which fits the configuration of the levo form better than it does that of the dextro modification.

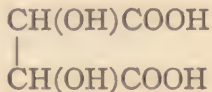
A very large proportion of the compounds of which living organisms are composed contain one or more asymmetric carbon atoms. It seems quite probable that the differences this property makes possible may have a great deal to do with specific differences among plants and animals.

**Malic Acid.**—There are a few other hydroxy acids that are of sufficient importance to warrant a brief discussion. Malic acid contains one hydroxyl group and two carboxyl groups. Its structural formula is:

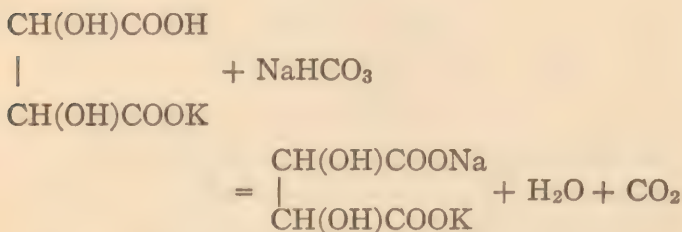


It is succinic acid, in which one hydrogen atom has been replaced by an hydroxyl group. Malic acid is very widely distributed in fruits. It is especially abundant in the berries of the mountain ash, and in unripe apples, from which it received its name. It is formed in certain cacti as an intermediate product in the oxidation of sugars. It accumulates during the night to be oxidized further to carbon dioxide and water during the day. Malic acid is a crystalline solid which is very soluble in water. Its molecule contains one asymmetric carbon atom, and it therefore exists in two optically active forms. The malic acid occurring in fruits is dextrorotatory in concentrated solutions.

**Tartaric Acid.**—The structure of tartaric acid is very similar to that of malic acid, except that one of the hydrogen atoms combined with another of the carbon atoms has also been replaced by an hydroxyl group. Its formula is



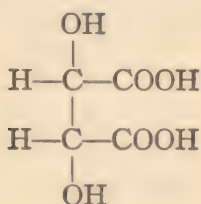
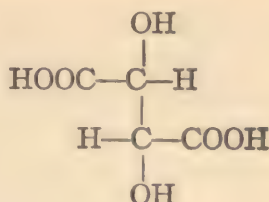
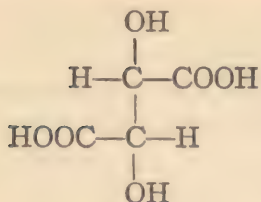
This acid is even more widely distributed in plants than is malic acid. It is especially abundant in grapes, from which it is prepared commercially. The acid and its salts are used in dyeing. The potassium acid salt, cream of tartar, is a constituent of certain baking powders, in which it is mixed with sodium acid carbonate. When moistened, these two salts react as follows:



The potassium sodium salt thus formed is called Rochelle salt. It is used as a reagent in the laboratory, and in medicine. The potassium antimonyl salt, tartar emetic, is also used in medicine.

Tartaric acid is of especial interest because it was in this compound that Pasteur first observed the phenomenon of optical activity. The explanation of it, as being due to the presence of asymmetric carbon atoms, was given later, independently, by LeBel and van't Hoff.

This acid contains two asymmetric carbon atoms; and three different structures, shown in the figures below, are possible:

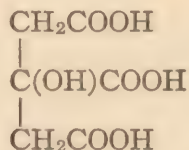


The first and second of these are optically active, one dextrorotatory and the other levorotatory. A mixture of equal parts of these two forms is inactive, and is sometimes called racemic acid. The third form, meso-tartaric acid, is inactive by internal compensation. That is, the arrangement of the groups around one of the carbon atoms is such as to rotate the plane of polarized light to the right, the other is so arranged as to rotate it to the left. The result is that no rotation occurs, and the compound is inactive.

If the groups combined with one of the carbon atoms of tartaric acid were not identical with those combined with the other, still another arrangement would be possible. In general, the number of arrangements of a compound possible is equal to 2 raised to the  $n$ th power, in which  $n$  is the number of asymmetric carbon atoms in the molecule. This would give four possibilities for tartaric acid, but, as the groups around

the two asymmetric carbon atoms are identical, only three arrangements are possible.

**Citric Acid.**—Another acid which occurs in many fruits is citric acid. It has the following structure:



It is, then, a tribasic acid and a tertiary alcohol. It is especially abundant in the juices of the citrus fruits and is prepared commercially from lemons. The acid is used in making artificial lemonades and other soft drinks. Some of its salts are used in analytical chemistry and in dyeing. It is a crystalline solid, having a sharp sour taste like lemons. It contains no asymmetric carbon atoms, and therefore exists in only one form.



## CHAPTER VIII

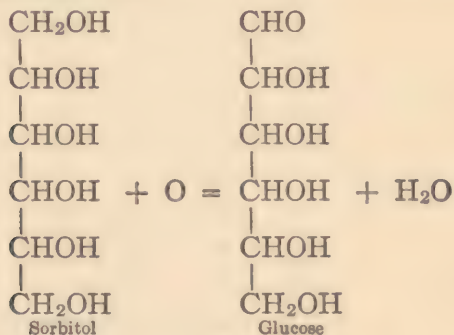
### THE CARBOHYDRATES

A very interesting and important group of the mixed compounds includes those that are both alcohols and either aldehydes or ketones. These may be considered as derived from the polyhydric alcohols by the oxidation of a primary alcohol group to aldehyde, or of a secondary alcohol group to ketone. The simplest compound that corresponds with this description

is glycol aldehyde,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CHO} \end{array}$ , which has been mentioned

as the first product of the oxidation of the dihydric alcohol glycol (page 96). Glycol aldehyde itself occurs very rarely, if at all, in nature, but several compounds of the same general nature are very widely distributed.

**Glucose.**—The oxidation of one of the primary alcohol groups of the hexahydric alcohol sorbitol yields an aldehyde, glucose:

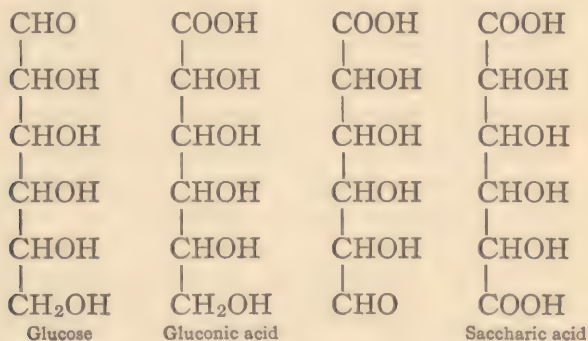


There are four asymmetric carbon atoms in this molecule, and therefore sixteen compounds having this formula are possible. Glucose is one of these. It is by far the most important of the compounds of this type, which are called the sugars. In the animal body, glucose is found in the blood and in the muscles, where it is oxidized to furnish heat, and energy for work. It is almost universally distributed in plants, although it does not usually occur in very large amounts. It is an intermediate compound in the chemical changes taking place in plants, and is oxidized to furnish the energy required for the activities of the plant. Glucose is prepared commercially by the action of acids on starch. It is the chief constituent of corn sirups.

**Specific Rotatory Power.**—Glucose is a white crystalline solid which is quite soluble in water, but not very sweet. Its solution rotates the plane of polarized light to the right. The action of a compound on polarized light is stated in terms of the direction and degree to which the light would be rotated on passing through a column ten centimeters long of a solution containing one gram of the substance in each cubic centimeter. This is called the specific rotatory power of the compound. For glucose this is  $52.5^\circ$  to the right, or  $+52.5^\circ$ , as it is usually written.

**Oxidation.**—The oxidation of glucose is its most important chemical reaction. It is by this means that it serves its principal function in living organisms. Under suitable conditions, glucose may be oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and this happens in living cells. Many intermediate products are formed before the comple-

tion of this change. In any given case, the products formed depend on the strength and nature of the oxidizing agent, how long it acts on the sugar, and the temperature. First, the aldehyde group is oxidized to carboxyl. Next, the primary alcohol group is oxidized to aldehyde, then to acid. These three steps in the oxidation of glucose are shown in the formulas below:



Further oxidation would form ketone groups from some of the secondary alcohol groups. The compounds formed in this way are very unstable, and the molecule falls to pieces. Acids containing less than six carbon atoms are formed, and, if the oxidizing agent is powerful enough, these are oxidized to CO<sub>2</sub> and H<sub>2</sub>O. In alkaline solutions sugars are oxidized much more rapidly than in acid or neutral solutions. The alkali seems to break the sugar molecule into fragments which take up oxygen very readily. The oxygen of the air is sufficient to cause a very considerable change in an alkaline solution of glucose.

**Fehling's Solution.**—As glucose is oxidized so readily, it is a good reducing agent. Alkaline solutions of certain metals, such as silver and copper, are reduced by glucose just as they are by other aldehydes. The ability of glucose to reduce cupric, or divalent copper to the cuprous, or monovalent, condition, is made use of in the quantitative determination of this sugar. For this purpose a solution of copper sulfate is mixed with a strongly alkaline solution of sodium potassium tartrate. The copper hydroxide formed is kept from precipitating by combining with the tartrate to form a complex soluble salt. This mixture is called Fehling's solution. When heated with glucose, cupric hydroxide is reduced to cuprous hydroxide:

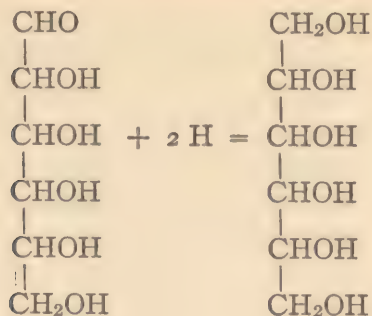


Cuprous hydroxide is unstable and decomposes to cuprous oxide and water:



The bright red cuprous oxide is precipitated and may be filtered off and its amount determined. The amount of cuprous oxide formed by a given amount of glucose depends on the concentration of the solution and on the length of time of heating. These conditions must, therefore, be kept constant in all determinations of this kind.

**Reduction and Ether Formation.**—Like other aldehydes, glucose is reduced to the corresponding alcohol, in this case sorbitol, when treated with nascent hydrogen:



In living organisms, still further reduction of glucose occurs and fats are formed. The details of this change are not well understood.

One of the hydroxyl groups of glucose may combine with an hydroxyl group of another compound to form an ether. The resulting compounds, called glucosides, will be discussed briefly in a later paragraph.

**Fermentation.**—The production of alcohol and carbon dioxide by the action of yeast on glucose has been mentioned. This change is caused by a catalytic agent, called zymase, which is secreted by the yeast cells. Many other microorganisms and even the higher plants are able to cause this change under some conditions. A small amount of energy is liberated during this fermentation. This is one way in which organisms that are not able to obtain oxygen may be able to get part of the energy they require.

**Galactose.**—At least fourteen of the sixteen sugars having the same formula as glucose have been prepared. There are only two of them beside glucose that are known to occur in nature. Of these the more

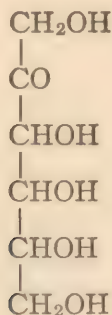


important is galactose. It occurs combined with glucose in lactose, the sugar of milk. It is quite widely distributed in gums and other substances occurring in plants, and it is a constituent of nervous tissue.

In both physical and chemical properties, galactose is very much like glucose. Its specific rotatory power is  $+81.5^{\circ}$ . It is fermented by yeast, but much more slowly than is glucose, and reduces metallic solutions somewhat more easily than glucose.

**Mannose.**—Mannose, another sugar having the same formula as glucose, is fairly widely distributed in plants combined with other substances. It occurs in especially large amounts in the ivory nut and in date seeds. It resembles glucose and galactose very closely in most of its properties. Its specific rotatory power is  $+14.6^{\circ}$ .

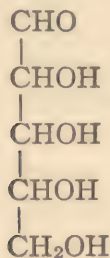
**Fructose.**—A large number of ketones might be formed by the oxidation of one or another of the secondary alcohol groups of the hexahydric alcohols. Only one of these compounds, fructose, occurs naturally in any considerable amounts. Its formula is



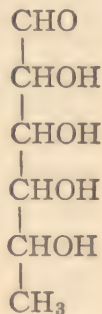
This sugar is very widely distributed, occurring along with glucose in honey, in many fruits, and in the leaves of many plants. It may be prepared by the action of acids on inulin, a substance quite similar to starch.

Fructose differs from glucose in only a few of its properties. It is sweeter than glucose, and it is levorotatory; its specific rotatory power is  $-92.3^\circ$ . It is the least stable of the sugars and is decomposed by both acids and alkalies. It reduces alkaline solutions of copper more readily than glucose, but does not cause quite so much reduction. It is fermented readily by yeast.

**Pentoses.**—The aldehyde formed by the oxidation of one of the primary alcohol groups of the pentahydric alcohol xylitol has the formula shown below. Three of the carbon atoms are asymmetric, and eight compounds having this formula are possible.



Xylose



Rhamnose

Two of these are quite widely distributed in nature. Arabinose occurs combined with other sugars in the vegetable gums, such as gum arabic. Xylose is one

of the constituents of the very complex substances that comprise the woody tissue of plants. Rhamnose is like arabinose and xylose except that one of the hydrogens of the primary alcohol group has been replaced by the methyl group. It occurs in some of the glucosides.

**Definition of Carbohydrate.**—All the compounds discussed so far in this chapter belong to a large and important group of substances called the carbohydrates. Though the carbohydrates are very important in animal nutrition, they are very much more abundant in plants.

Most carbohydrates contain hydrogen and oxygen in the same proportion in which they occur in water. It was for this reason that they were given the name meaning hydrates of carbon. Not all the carbohydrates, however, have this composition. Rhamnose,  $C_6H_{12}O_5$ , is one which does not. All the carbohydrates contain an alcohol group and a carbonyl group combined directly with each other. Thus the structure

$$\begin{array}{c} | \\ \text{CHOH} \\ | \\ \text{CO} \\ | \end{array}$$
 is common to all the carbohydrates. This

structure may be obtained by the oxidation of any polyhydric alcohol. The carbohydrates may be defined, then, as aldehyde or ketone derivatives of the polyhydric alcohols.

**The Monosaccharides.**—All of the carbohydrates so far studied contain only one of these characteristic groups. For this reason they are called the monosac-

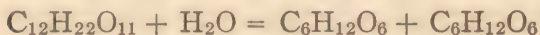
charides. This group is subdivided on the basis of the number of carbon atoms in the molecule. Of those mentioned, glycolaldehyde is a biose; xylose and arabinose are pentoses (rhamnose is a methyl pentose); glucose, galactose, mannose, and fructose are hexoses. At least two heptoses have been discovered lately, but they do not appear to be of much importance. Octoses, nonoses, and decoses have been prepared in the laboratory.

**Sucrose.**—Sucrose, or cane sugar, is one of the best known of the carbohydrates. It is almost universally distributed among the higher plants, where it is usually mixed with glucose and fructose. It occurs in especially large amounts in the juices of the sugar cane and the sugar beet, and it is principally from these sources that it is prepared commercially. Quite large amounts of sucrose are found in the sap of the hard maple and of other trees. Smaller amounts are found in the juices of most plants, and it is widely distributed in seeds.

The best commercial grades of sucrose are very pure, so that no description of its appearance, solubility, or taste is needed here. It is optically active, having a specific rotatory power of  $+66.7^\circ$ . This property is often used in the quantitative determination of sucrose.

**Chemical Properties: Hydrolysis.**—Sucrose is very much more stable than the sugars previously mentioned. It is not fermented by yeast, and it does not reduce Fehling's solution. For these reasons it appears that it does not contain a free aldehyde or

ketone group. However, if a solution of sucrose is heated with a little acid, and the acid is then neutralized, the resulting solution reduces Fehling's solution, and is fermented by yeast very readily. An examination of this solution shows that it no longer contains sucrose, but instead, a mixture of equal parts of glucose and fructose. The formula representing the percentage composition and the molecular weight of sucrose is  $C_{12}H_{22}O_{11}$ . That for both glucose and fructose is  $C_6H_{12}O_6$ . During the heating of the solution, each molecule of sucrose has taken up a molecule of water, and decomposed into two simpler molecules, one of glucose and one of fructose. The acid has acted only as a catalytic agent. This reaction is another example of hydrolysis, the decomposition of a molecule into two or more parts with the addition of the elements of water:



**Condensation.**—Under certain conditions, especially in living plants, the reverse of this reaction takes place, that is, a molecule each of glucose and fructose are combined with the loss of a molecule of water to form a molecule of sucrose. This is very like the formation of an ester from an acid and an alcohol, only the product is not an ester. As a general name for all these reactions that are the reverse of hydrolysis, the term "condensation" may be used. In this sense, condensation is the union of two or more molecules with the elimination of water. A very large



part of the chemical reactions that take place in living organisms are of these two opposite types, hydrolysis and condensation.

It is evident, from the properties of sucrose, that in its formation glucose and fructose are combined in such a way that both of the carbonyl groups are rendered inactive. It is to this fact that sucrose owes its relative stability. Just how the two simpler molecules are combined is somewhat uncertain as yet. It appears that the carbonyl groups are latent and are easily reformed on hydrolysis.

**Fermentation.**—It has been said that sucrose is not fermented by yeast, but old cultures of yeast produce a catalytic agent which favors the hydrolysis of sucrose. If subjected to the action of such yeast, sucrose is hydrolyzed, and the glucose and fructose formed are then fermented.

**Inversion.**—Sucrose in solution rotates the plane of polarized light to the right. Of the products of its hydrolysis, glucose is dextrorotatory, but fructose is levorotatory to a still greater degree. The direction of rotation has been reversed, or inverted. For this reason the hydrolysis of sucrose is often called inversion.

**The Disaccharides.**—Since sucrose is formed by the combination of two monosaccharides, glucose and fructose, it is called a disaccharide. Several other sugars are formed in a similar way and therefore are classed as disaccharides. Only two of them will be mentioned. Both of them are formed by the condensation of two hexoses, and both have the same

composition and molecular weight as sucrose, corresponding to the formula  $C_{12}H_{22}O_{11}$ .

**Maltose.**—Maltose, one of these disaccharides, is an intermediate product in the formation of glucose from starch. Considerable amounts of it are found in corn sirups. Ordinarily it does not occur in very large amounts in nature, but it is formed abundantly during the germination of certain seeds, such as barley.

Maltose is very active optically, having a specific rotatory power of  $+137^\circ$ . Chemically it differs from sucrose in reducing Fehling's solution. Thus it contains a free carbonyl group. On hydrolysis two molecules of glucose are formed from each molecule of maltose. Maltose is formed, then, by the condensation of glucose alone.

**Lactose.**—Lactose is the sugar that occurs in milk. It is a disaccharide, having the same formula as sucrose and maltose,  $C_{12}H_{22}O_{11}$ . It is prepared commercially from whey, and is used in the manufacture of infants' foods and medicines. Its specific rotatory power is  $+52.5^\circ$ . It is not nearly as sweet as sucrose.

Lactose is not fermented by yeast, but it reduces Fehling's solution, and therefore contains a free carbonyl group. When heated with acids, it is hydrolyzed much more slowly than sucrose, and equal parts of glucose and galactose are formed. Lactose, then, is a product of the condensation of glucose and galactose.

**The Polysaccharides.**—The carbohydrates studied so far are soluble, sweet, crystalline compounds of known molecular weight. They are called the

sugars. A few trisaccharides of rather rare occurrence also belong to this group. Most of the carbohydrates found in nature, however, are insoluble, or form colloidal solutions. They are not sweet, and, although their percentage composition is known, their molecular weight has not been determined. It is undoubtedly very large. On heating with acids they are hydrolyzed with more or less difficulty, and the final products of their hydrolysis are one or more monosaccharides. They are, then, condensation products of many monosaccharide molecules, and for this reason they are called the polysaccharides.

**Starch.**—One of the best known and most important of these substances is starch. Its percentage composition is represented by the formula  $C_6H_{10}O_5$ , but its structure is undoubtedly much more complex than this, and its formula is usually written  $(C_6H_{10}O_5)_x$ .

Starch does not occur in animals, but it is very widely distributed in plants, where it is found in leaves, and in various organs in which food is stored, such as roots, tubers, seeds, and stems. It occurs in the form of small grains whose size, shape, and structure are more or less characteristic of the species of plant by which they are formed.

Starch forms a very important part of the food of animals. It is especially abundant in the seeds of the cereals such as corn, wheat, oats, rye, barley, and rice, and in certain tubers and roots such as potato and arrowroot. In somewhat smaller amounts it occurs in most of our vegetable foods. It is prepared com-

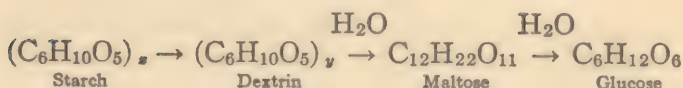
mercially in this country mostly from corn; in Europe, principally from potatoes. Arrowroot and rice also are used to some extent as sources of starch.

**Properties.**—Starch is insoluble in water, but when boiled for a short time the small grains burst and part of their contents forms a colloidal solution which is called starch paste. Starch gives a deep blue color with iodine which is quite characteristic, and which is often used as a qualitative test for starch.

When dry starch is heated to about  $200^{\circ}$ , dextrin is formed. Dextrin dissolves in water forming a viscous solution which has adhesive properties. It is used in making confectionery, in calico printing, and as an adhesive on postage stamps and envelopes. The peculiar character and flavor of the crust of bread and of toast are due, in part at least, to the formation of dextrin from starch. Dextrin is formed also when cloth that has been starched is ironed.

**Hydrolysis.**—When starch is heated with acids, the changes that occur are rather complex. First the molecule seems to be broken into smaller parts still having the same percentage composition as the original starch. The compounds formed are called dextrans. There are probably several of these dextrans but the exact number of them is not known. If the heating is continued, hydrolysis begins and the first recognizable product is maltose. Of course the next step, which is the final one, results in the formation of glucose, since this is the only product of the hydrolysis of maltose. These changes may be represented roughly as follows:





The various stages in the reaction are not as sharply defined as the above scheme would indicate. Some maltose, and even some glucose, may be formed before all the starch has been converted into dextrin. During the course of the hydrolysis, the amounts of the more complex substances decrease gradually and the amount of the simpler product, glucose, increases until finally the change to glucose is complete. The action of acids on starch is used commercially in the preparation of corn sirups. The change is not carried to completion, so the sirup contains maltose and dextrans as well as glucose. Sucrose is often added to improve the flavor. Glucose is prepared commercially in the same way, except that the hydrolysis is more complete, and the solid sugar is separated. During the digestion of starch in foods, changes very similar to those caused by acids are brought about by catalytic agents present in the digestive fluids. In this way starch is changed completely to glucose.

**Starch in Plants.**—In the leaves of green plants, sugars are formed during the day. In most of these plants, part of the sugar formed is condensed to starch and stored temporarily in the leaf. This starch is gradually hydrolyzed to sugar again, and carried in solution in the sap to other parts of the plant, where it is used to build new structures, or stored, again in the form of starch, for future use.

**Glycogen.**—Glycogen is a polysaccharide which



is similar in many respects to starch. It is the form in which carbohydrates are stored in animals. For this reason it is sometimes called animal starch. It is especially abundant in the liver and muscles, though the amount present varies widely. It is greatest soon after a meal that is rich in carbohydrates. It also occurs in scallops, in yeast, and in certain fungi.

Glycogen does not occur in the form of grains, as starch does, but is an amorphous white powder which dissolves in water, giving an opalescent colloidal solution, which gives a red color with iodine. A peculiar property of glycogen is that it is very resistant to the action of alkali. It may be separated from the tissues in which it occurs by destroying the tissues by boiling them with very concentrated alkali, a treatment which seems to have no effect on the glycogen. It is hydrolyzed very readily by acids, forming intermediate products similar to those formed from starch. The final product of its hydrolysis is glucose. It is, then, a condensation product of glucose, and its formula, like that of starch, is  $(C_6H_{10}O_5)_x$ .

**Inulin.**—In the dahlia, the artichoke, and some other plants mostly belonging to the family Compositae, carbohydrate is stored in the form of inulin instead of starch. Inulin is a white powder which is slightly soluble in cold water and very soluble in hot water. It has the same formula as starch  $(C_6H_{10}O_5)_x$ . When it is heated with acids, it is hydrolyzed to fructose, of which it is, therefore, a condensation product.

**Cellulose.**—Starch, glycogen, and inulin all are formed in living organisms by the condensation of

simple sugars. They are stored temporarily, later to be hydrolyzed to sugars again and used as food. Another polysaccharide, cellulose, also is formed by the condensation of simple sugars, but, instead of being stored for future use, it forms the framework of plants, and is not available for further use as food. Cellulose is rarely found in even an approximately pure condition, but it is combined or mixed with other substances, some of which will be mentioned later. The best grades of filter paper are nearly pure cellulose from which the impurities have been removed in the process of manufacture. Among the natural products, cotton fiber is the best known example of nearly pure cellulose. In its various forms of combination, cellulose is one of the most abundant of the products of plants. Wood, and all the vegetable fibers, such as cotton, linen, and hemp are composed largely of this substance.

**Properties.**—Cellulose is characterized by its extreme resistance to chemical action. It is insoluble in all the ordinary solvents, but may be dissolved, apparently without decomposition, in an ammoniacal solution of copper hydroxide (Schweitzer's Reagent). When this solution is made acid, the cellulose is precipitated. Under suitable conditions, the cellulose may be separated in the form of threads which have a silky luster. This is one of the methods used in the manufacture of artificial silk. A solution of zinc chloride in hydrochloric acid also dissolves cellulose, but some decomposition probably occurs. If cotton fiber is treated with fairly concentrated sodium hydroxide, the fibers shrink and become more transparent. The alkali

may be washed out and the fiber used for the manufacture of cloth which is called mercerized cotton. If the alkali cotton mixture is treated with carbon bisulfide, a compound called cellulose xanthate is formed, which is used as an intermediate substance in the making of moldings and of very tough and resistant films. In making these products, the carbon disulfide, is removed, regenerating the cellulose.

Nitric acid combines with the free alcoholic hydroxyl groups of cellulose forming esters which are of great commercial importance. The number of hydroxyl groups with which the acid combines is usually stated on the basis of a cellulose molecule containing twelve carbon atoms. Nitrates as high as the hexanitrate may be formed, the number depending on the strength of the acid used and the length of time it acts. The nitrates of cellulose all burn very easily, and the higher ones are extremely explosive. These are called gun cotton. Dissolved in the proper solvents, the nitrates may be precipitated as fibers. The nitrate groups are removed to make the material less inflammable, and the fibers are used for making artificial silk. The lower nitrates of cellulose are dissolved in a mixture of alcohol and ether forming collodion, and celluloid is made by mixing them with camphor.

When cellulose is treated with fairly concentrated sulfuric acid, a tough substance called amyloid is formed, which may be used as a substitute for parchment. If it is boiled for a long time with sulfuric acid, cellulose is hydrolyzed completely to glucose. It is, then, a condensation product of glucose, just as is starch. Its composition, like that of starch, is repre-

sented by the formula  $(C_6H_{10}O_5)_x$ . Because of its much greater resistance to hydrolysis, it is evident that the glucose molecules of which it is composed, are combined in a different way from those in starch.

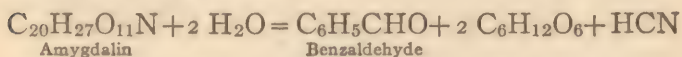
**Hemicelluloses.**—In many plants, substances resembling cellulose in their location and in some of their properties occur. These substances are much less resistant to hydrolysis than cellulose. They have, at least to some extent, the function of reserve food substances, being dissolved and used by the plant in building new structures. They are of some value as food for animals, especially for the herbivorous animals. Because they resemble cellulose, but are so much more easily hydrolyzed, they are called hemicelluloses. The hemicelluloses occurring in different plants differ somewhat in their composition, and different sugars are formed by their hydrolysis. Glucose, galactose, mannose, xylose, and arabinose are among the products of hydrolysis of these substances. The hemicelluloses may be considered to be intermediate between such carbohydrates as starch and inulin, which are purely reserve substances, and cellulose, which is not capable of being used again, but serves only as the supporting framework of plants.

**Compound Carbohydrates.**—Besides occurring alone, carbohydrates are often found combined with other substances. The compounds with which the carbohydrates are combined belong to no single group, but are quite varied, and the resulting complexes differ widely in their nature and properties. For convenience they may be classed together as Compound Carbohydrates. A few of them will be mentioned briefly.

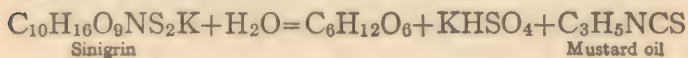


**Glucosides.**—Glucose, and, to some extent, others of the simple sugars, form etherlike compounds with a great variety of substances. An hydroxyl group of the sugar and one of the other compound unite with the elimination of a molecule of water, just as two molecules of ethyl alcohol unite to form ethyl ether. The compounds formed in this way are called glucosides. As a matter of fact, the sugars combine with each other in this way, and the disaccharides are really glucosides. By this term is usually meant, however, a sugar combined with a nonsugar. A wide variety of compounds may be combined in this way. Practically the only property common to all the glucosides is the production of a sugar on hydrolysis. Two examples of these substances will be given.

**Amygdalin.**—Amygdalin is a compound which is found in bitter almonds, peach stones, and cherry pits. A catalytic substance also is present, which hastens the hydrolysis of amygdalin, but it does not act until the cells have been broken or their walls decomposed. Amygdalin is readily hydrolyzed by acids. The products formed by its hydrolysis are glucose, benzaldehyde, and hydrocyanic acid. The following equation illustrates this reaction:



**Sinigrin.**—Sinigrin is a glucoside which occurs in the seed of black mustard. On hydrolysis it yields glucose, potassium hydrogen sulfate, and allyl isothiocyanate (mustard oil):





Some sixty or more glucosides are known. Most of them yield glucose on hydrolysis, but some contain arabinose, rhamnose, or other sugars. Some of the glucosides are quite poisonous. Their functions in plants are not known.

**Tannins.**—The tannins are complex substances which are very widely distributed in plants. Most of them are compounds of sugars with more or less complex aromatic compounds. They occur especially in the bark of certain trees, but also in leaves and other parts of plants. They occur in large amounts in the galls that are formed by the action of certain insects on plants. The tannins are very astringent, and make unfit for food many plant parts that would otherwise be valuable for this purpose.

Most of the tannins are soluble in water. They form blue-black or greenish compounds with iron salts, and for this reason were formerly used in the manufacture of ink. They are strongly reducing substances, and therefore, must be removed from plant extracts before the amount of reducing sugars present can be determined. Many of the tannins form very tough and resistant compounds with proteins. Such compounds are formed with the proteins of skins when they are tanned. The bark of certain trees is used largely as a source of tannin for this purpose.

**The Pectins.**—The pectins contain a number of sugar molecules grouped around a complex organic acid. They are very widely distributed, especially in certain fruits and vegetables. It is the presence of pectins that causes the juices of some fruits to form

jellies. Some fruit juices which do not contain enough pectins may be made to form jellies by the addition of pectin obtained from other fruits or vegetables.

**Gums and Mucilages.**—Although differing considerably in physical properties, the gums are quite like the pectins in composition. They consist of a number of sugar molecules grouped around a complex organic acid. In both pectins and gums, the sugars most frequently found are galactose and arabinose. Some of the gums are quite important commercially. Thus gum arabic, which is a white solid, is used as an emulsifying and deflocculating agent in many preparations. The vegetable mucilages are slimy substances, which appear to have a composition quite similar to that of the gums.

**The Compound Celluloses.**—The most important of the compound carbohydrates are those of which cellulose is a constituent. After the formation of true cellulose in plants, it often becomes modified by combination or admixture with other substances which modify its properties. The most important of these modifying substances is lignin. The ligno-celluloses so formed comprise the woody tissue of plants. The chemical nature of lignin is not known definitely, but it is considerably more active chemically than cellulose. The direct uses of wood are too well known to require mention. Immense quantities of it are used in making paper. For this purpose, it is necessary to free the wood, as far as possible, from lignin, thus leaving nearly pure cellulose. The method most commonly used is to heat the wood with  $\text{Ca}(\text{HSO}_3)_2$ . This dis-

solves the lignin, leaving the cellulose nearly unaffected. For the cheaper grades of paper, the treatment is not continued long enough to remove nearly all the lignin, and such paper soon turns yellow on exposure to light. By more thorough and careful treatment, very fine grades of paper may be produced.

Cellulose combined or mixed with certain waxy substances is called adipocellulose or cutocellulose. This is very resistant, and forms the protective covering of many parts of plants.

#### OUTLINE CLASSIFICATION OF THE CARBOHYDRATES

Monosaccharides	{	Biose	Glycol aldehyde
		Pentoses	{ Arabinose Xylose
		Hexoses	{ Aldehydes { Glucose Mannose Galactose Ketone Fructose
Disaccharides	{	Sucrose	Yield on hydrolysis Glucose and fructose
		Lactose	Glucose and galactose
		Maltose	Glucose
Polysaccharides	{	Starch	Glucose
		Dextrin	Glucose
		Glycogen	Glucose
		Inulin	Fructose
		Cellulose	Glucose
		Hemicelluloses	Hexoses and pentoses
Compound carbohydrates	{	Glucosides	
		Tannins	
		Pectins	
		Gums and mucilages	
		Lignocellulose	
		Cutocellulose	

## CHAPTER IX

### UNSATURATED AND AROMATIC COMPOUNDS

When ethyl chloride is treated with an alkali, such as silver hydroxide, ethyl alcohol is formed:



But if potassium hydroxide in hot alcoholic solution is used, quite a different change occurs:



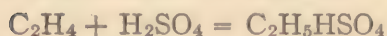
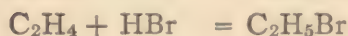
The hydrocarbon formed is ethylene, a colorless gas with a peculiar sweet smell. It is among the products formed by the destructive distillation of organic substances. Coal gas contains about 6 per cent of this hydrocarbon. It burns with a flame that is much more luminous than that given by ethane, and it is highly explosive. It is not very toxic to animals, but for some reason it is extremely injurious to plants. A little coal gas escaping in a greenhouse may have very serious results, and it has been shown that the injury is due to the ethylene present in the gas.

**Properties.**—It will be noticed that ethylene resembles ethane quite closely in composition but that its molecule contains two less hydrogen atoms. It is

evident that the structure of this compound must differ

from that of ethane. The formula,  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{HC} - \text{CH} \end{array}$ , would account for only three of the valences of the carbon atoms and therefore it must be incorrect. All the properties of ethylene indicate that the carbon atoms are joined by two valences, instead of by only one.

Its formula would be  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{HC} = \text{CH} \end{array}$ . This double bond between the carbon atoms does not join them more firmly than a single one, but much less so. A compound containing a double bond is said to be unsaturated. It can form addition products, which it is impossible for such compounds as ethane and its homologs to do. The following equations illustrate reactions in which ethylene forms addition products:



The double bond between the carbon atoms opens, and a monovalent atom or group of atoms is added to each of the carbon atoms. It will be seen that the products of these reactions are ethane or its derivatives. In other words, by addition reactions unsaturated compounds are changed to the corresponding saturated compounds. Due to this property, the unsaturated compounds are much more active chemically, and much



less stable than the saturated. There is quite a tendency for the molecule to fall apart at the double bond.

**Homologs and Derivatives.**—Ethylene is the first member of an homologous series of hydrocarbons called the Ethylene or Olefin Series. Just as with the paraffin series, each member may be considered as derived from the preceding one by the substitution of a  $\text{CH}_3$ — group for one of the hydrogens; each member of the series would contain two less hydrogen atoms than the corresponding member of the paraffin series, that is each member contains one double bond. The general formula for the series is  $\text{C}_n\text{H}_{2n}$ , and the common difference,  $\text{CH}_2$ .

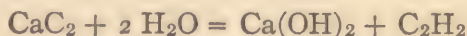
Just as other series of compounds, such as the halogen substitution products, alcohols, aldehydes, and acids, may be derived from the paraffin hydrocarbons, so similar series may be derived from the olefin hydrocarbons. However, very few of these unsaturated compounds are of any importance from a physiological point of view. The most important of them is oleic acid,  $\text{C}_{17}\text{H}_{33}\text{COOH}$ , which has been described as a constituent of the fats and oils. Due to the double bond in its molecule, this acid is able to add hydrogen, iodine, and oxygen. The hydrogenation, or hardening, of the vegetable oils is an example of the use of this property.

**Acetylene.**—Acetylene,  $\text{C}_2\text{H}_2$ , is an hydrocarbon which is formed along with other products, when an electric arc is passed between carbon poles in an atmosphere of hydrogen. It is prepared commercially

by the action of water on calcium carbide. The carbide is prepared by heating lime and carbon together:



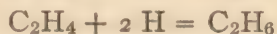
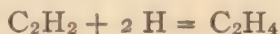
When the carbide is treated with water, the following reaction occurs:



Acetylene is a colorless gas with a garliclike odor. It burns with a smoky flame, but in especially constructed burners it gives a very brilliant light and a very high temperature. When mixed with the proper proportion of oxygen, it burns with such a hot flame that it is used in cutting metals. Even when not mixed with oxygen or air, acetylene is extremely explosive. It is dangerous to store it under pressure, and many serious accidents have resulted from attempts to do this. There are conditions, however, under which it may be stored safely, even under high pressure. For this purpose tanks are used which are filled loosely with asbestos or some other fiber, soaked in acetone. It is in such tanks that acetylene is put on the market.

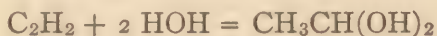
**Chemical Properties.**—To account for the four valences of the carbon atoms in acetylene it is necessary to assume that the two carbon atoms are joined by three bonds. Its structural formula is  $\text{HC}\equiv\text{CH}$ . The properties of acetylene show that this assumption is correct. This compound is still more highly unsaturated than ethylene. One or both of the extra valences may open and add two monovalent atoms or groups.

Hydrogen may be added in two steps as is shown in the following equations:

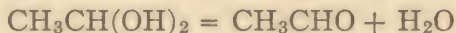


Thus by the partial saturation of acetylene, ethylene or its derivatives may be formed, and complete saturation leads to the formation of ethane or its derivatives.

A very interesting application of this property of acetylene has been developed quite recently. In the presence of a suitable catalyst, acetylene will add two molecules of water. A molecule of water dissociates into two parts,  $\text{H}-$  and  $-\text{OH}$ .



Both of the  $-\text{OH}$  groups add to the same carbon atom. The product of this reaction will be recognized as identical with the first step in the oxidation of ethyl alcohol to acetaldehyde (page 41). It is very unstable because two hydroxyl groups are combined with the same carbon atom, and immediately loses a molecule of water, forming acetaldehyde:



The aldehyde formed is oxidized very easily to acetic acid, and it may be reduced fairly easily to alcohol. Thus a means is furnished for the large scale production of these compounds which are of such great commercial importance. It is entirely possible

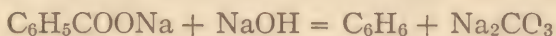
that, where waterfalls furnish a cheap source of electricity for the manufacture of acetylene, this method for the preparation of acetic acid and alcohol may compete with the methods now used more commonly.

**Homologs and Derivatives.**—Acetylene is the first member of another homologous series of hydrocarbons, each of which contains a triple bond, and of which each may be considered as derived from the preceding member by the substitution of a  $\text{CH}_3$ —group for an atom of hydrogen. The general formula for this series is  $\text{C}_n\text{H}_{2n-2}$ , and the common difference, as in the other series, is  $\text{CH}_2$ .

Series of halogen substitution products, alcohols, aldehydes, and acids also may be derived from the acetylene series of hydrocarbons. All these compounds are very active chemically and quite unstable. By partial saturation they form derivatives of the olefins, and by complete saturation, derivatives of the paraffins. Few members of these series occur naturally, and they are not of sufficient physiological importance to warrant description here.

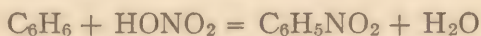
**Benzene.**—Under certain conditions, acetylene undergoes polymerization. If it is heated to redness in a closed tube, a liquid is formed which has the formula  $\text{C}_6\text{H}_6$ . It is, then, formed by the combination of three molecules of acetylene. This liquid hydrocarbon is called benzene. In the laboratory it may be prepared more conveniently by the same method used for the preparation of methane, which is a general method for the preparation of hydrocarbons. The acid derived from its next higher homolog is heated

with sodium hydroxide. In this case the acid used is benzoic acid, or rather, its sodium salt:



Along with a great many other substances, benzene is obtained as a by-product in the coking of coal. It is a colorless liquid, nearly insoluble in water, and burns with a smoky flame. It is used as a solvent and cleaner, but principally as a starting point in the manufacture of its many important derivatives, among which are some of the dyes and explosives.

**Structure, Properties, and Derivatives.**—Benzene is an unsaturated compound, but it is much more stable than such compounds usually are. All its properties lead to the conclusion that the six carbon atoms in its molecule are united in the form of a ring as is shown in the structural formula below. The three double bonds would indicate that addition products might be formed. It is possible to add six monovalent atoms or groups to the molecule. The terpenes, one of the groups of essential oils, are compounds of this kind. However, substitution compounds are formed much more readily. The ring structure seems to modify the activity of the double bonds. Nitric acid forms such a substitution product quite easily:



The product is a nitro compound (not a nitrite). It is called nitrobenzene, or oil of mirbane. It has an odor like that of oil of bitter almonds, for which it has been used as a substitute, but it is poisonous, and



should not be used as a flavoring material. When it is treated with nascent hydrogen, nitrobenzene, like other nitro compounds, is reduced to the corresponding amine:



This product is aniline, an oily liquid, slightly soluble in water. It is colorless when freshly prepared, but turns brown or black on standing. It may be considered as a substituted ammonia. Like ammonia,

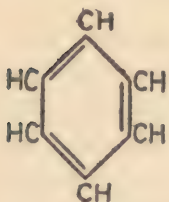


FIG. 8.—Benzene.

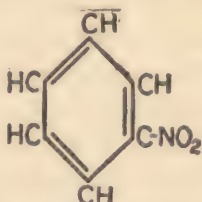


FIG. 9.—Nitrobenzene.

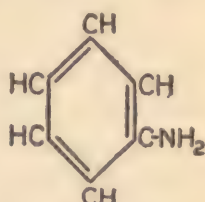
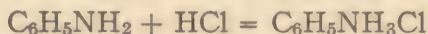
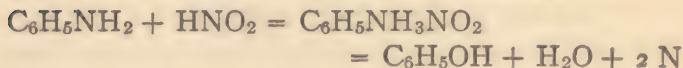
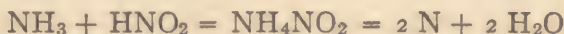


FIG. 10.—Aniline.

aniline is a base former, and it combines with acids to form salts just as ammonia does:



Aniline is the starting point in the synthesis of a great many of the dyes. When heated with  $\text{HNO}_2$ , it undergoes a reaction analogous to that of ammonia under the same conditions:

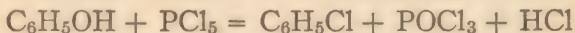


The final product of this reaction is phenol, or carbolic acid. It is obtained commercially as one of the products of the distillation of coal tar. Its use as a disinfectant is familiar, and large quantities are also used in the preparation of its derivatives, which include dyes, medicines, photo-developer, flavoring materials, and explosives.

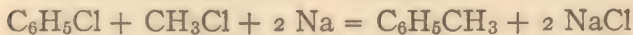
When pure, phenol is a colorless crystalline solid, but on exposure to light it turns pink, then brown or almost black. It is very corrosive and poisonous. Structurally phenol is an alcohol, but it is much more acid than basic in its properties, and neutralizes bases very readily:



This is true in general of compounds containing an —OH group substituted in a benzene ring. With  $\text{PCl}_5$  phenol reacts as the alcohols do, forming chlorbenzene:



**Toluene: The Side Chain.**—It is possible to replace the chlorine in this chlorbenzene with an alkyl radical by the same method that has been described for the synthesis of hydrocarbons (page —). Using methyl chloride, the reaction is indicated by the following equation:



The hydrocarbon formed in this case is toluene, a colorless liquid which is used as a preservative and solvent, and in the manufacture of the high explosive,

trinitrotoluene. It is a representative of a large number of compounds that are composed of a benzene ring and a side chain derived from paraffin or other open-chain hydrocarbons. The two parts of the molecule each retain, in large measure, their own chemical properties. Thus the side chain in toluene may be carried through the series of reactions characteristic of the paraffin hydrocarbons. On treatment with chlorine, one of the hydrogens of the  $\text{CH}_3$ — group may be replaced, forming benzyl chloride:

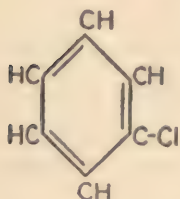
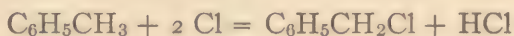


FIG. 11.—Chlorobenzene.

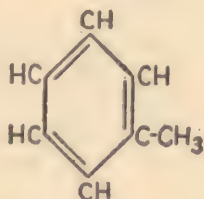


FIG. 12.—Toluene.

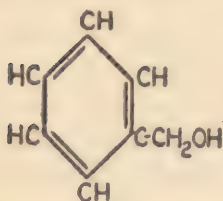


FIG. 13.—Benzyl alcohol.

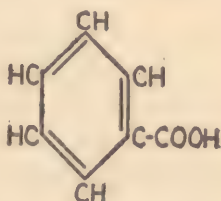
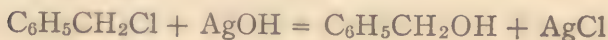


FIG. 14.—Benzoic acid.

On treating benzyl chloride with silver hydroxide, benzyl alcohol is formed:

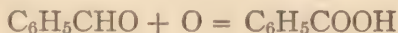


On the oxidation of benzyl alcohol, benzaldehyde is formed:



Benzaldehyde is a constituent of the glucoside amygdalin, occurring in bitter almonds and peach stones. It is called oil of bitter almonds and is used as a flavoring material.

On further oxidation, this aldehyde goes over to the corresponding acid:



The product, benzoic acid, is the compound mentioned as the starting point in one method for the preparation of benzene. Benzoic acid and its salts are sometimes used as preservatives of food products.

Salicylic acid,  $\text{C}_6\text{H}_4(\text{OH})\text{COOH}$ , a compound that combines the structure and properties of phenol and benzoic acid, occurs in the leaves and stems of tulips and hyacinths. Its methyl ester is oil of wintergreen, and the ester of its hydroxyl group with acetic acid is called aspirin. The acid is an antiseptic and is used as a food preservative. Its sodium salt and several others of its compounds, beside those mentioned above, are used in medicine.

**Derivatives of Benzene.**—More than one of the hydrogens of benzene may be replaced by other atoms or groups. Since each of these substituted groups may undergo various substitution and other reactions, it is evident that the possibility of the formation of different derivatives of benzene is practically limitless.

As a matter of fact, many more such compounds are known than the derivatives of the paraffin, olefin, and acetylene hydrocarbons combined. So important is the chemistry of these substances, and so characteristic are their reactions, that the cyclic compounds have been grouped together under the term aromatic compounds, to distinguish them from the open-chain compounds, which are called aliphatic. Several of the aromatic compounds occur in relatively small quantities in plants and animals, and many of them are used as medicines. They are, however, so much less important physiologically than the aliphatic compounds, that no further discussion of them will be given here. Their principal source is from the destructive distillation of coal, and their principal uses are the commercial ones already mentioned.



## CHAPTER X

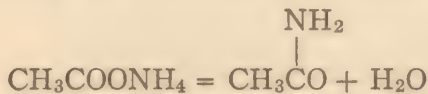
### NITROGEN COMPOUNDS

**Cyanides.**—The nature and uses of the cyanides of the metals will be remembered from the previous study of general chemistry. They are used in the extraction of certain ores, and potassium and sodium cyanides are used as sources of hydrocyanic acid with which trees and rooms are fumigated to destroy insects. Liquid hydrocyanic acid is now used directly for this purpose to some extent. When a cyanide is used, it is treated with an acid to liberate hydrocyanic acid.

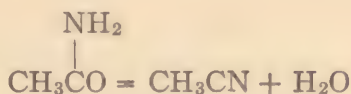
**Methyl Cyanide.**—Cyanides of organic radicals may be prepared. They are formed when an alkyl chloride is treated with potassium cyanide. With methyl chloride the reaction is as follows:



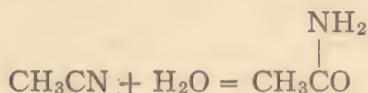
Methyl cyanide also may be prepared by the removal of water from ammonium acetate. This reaction takes place in two steps. The removal of one molecule of water results in the formation of acetamide:



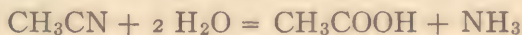
Further dehydration results in the formation of methyl cyanide:



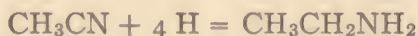
**Properties.**—Methyl cyanide is a liquid boiling at  $81^\circ$ . The second method given for its preparation may be reversed; if it is heated to a high temperature with water, one molecule of water is added, forming acetamide:



Heated in the presence of dilute acids the hydrolysis is complete, and acetic acid and ammonia are formed:



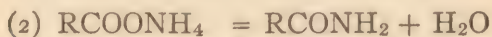
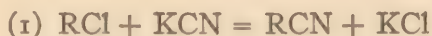
The reactions of methyl cyanide show that it has the following structure,  $\text{CH}_3\text{C}\equiv\text{N}$ ; it should be possible, then, to add four monovalent groups or atoms to the molecule. When it is treated with nascent hydrogen this occurs, and ethyl amine is formed:



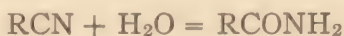
It should be noted that methyl cyanide is a derivative of methane, but the compounds formed from it, acetic acid and ethyl amine, are derivatives of ethane. In this fact lies the great importance of the cyanides in the synthesis of organic compounds, since it is possible, by the use of the reactions given, to prepare the

higher members of a series of compounds from the lower members.

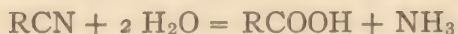
The methods of preparation given for methyl cyanide and the reactions it undergoes apply to all the organic cyanides. In the general form the equations for the preparation of cyanides may be given as follows:



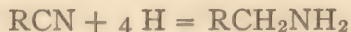
All the cyanides are changed by the action of water first to the corresponding amides:



and in the presence of dilute acids they are hydrolyzed:



Treated with nascent hydrogen, they are reduced to the corresponding primary amines:

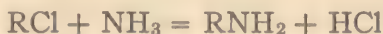


These reactions are used very extensively in the synthesis of organic compounds.

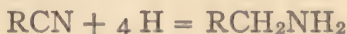
**Primary Amines.**—The primary amines may be considered as derived from ammonia by replacing one of the hydrogens by an alkyl radical. They are also derivatives of the hydrocarbons just as the chlorine substitution products and alcohols are. From

this point of view they may be considered to be derived by the substitution of a  $\text{—NH}_2$  group for one of the hydrogens of a hydrocarbon. Their general formula is  $\text{RNH}_2$ .

The primary amines may be prepared by heating a chlorine substitution product with ammonia in a closed tube at  $100^\circ$ :

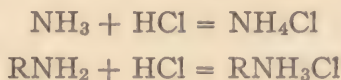


They may be prepared also by the reduction of cyanides:



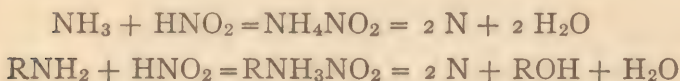
In general they are formed by the reduction of organic compounds in which nitrogen is combined directly with carbon. An example of such a reaction has been given in the formation of aniline by the reduction of nitrobenzene.

**Properties.**—The primary amines resemble ammonia very strikingly. Ethyl amine is a colorless liquid which smells quite like ammonia. They are stronger base formers than ammonia, and they form salts with acids just as ammonia does:



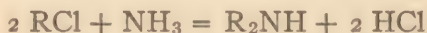
When heated with nitrous acid the primary amines behave in the same way as ammonia and aniline. This reaction has been described in a previous chapter. The

alcohol corresponding to the amine is formed and free nitrogen is liberated:

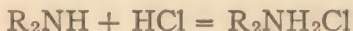


The amount of nitrogen liberated in this reaction serves as a measure of the amount of nitrogen present in the form of primary amines. This determination is very useful in many physiological studies.

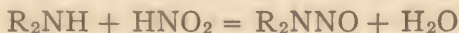
**Secondary Amines.**—The secondary amines are formed by replacing two of the hydrogens of ammonia by alkyl radicals. They are prepared by the first method given for primary amines, except that a larger proportion of the alkyl chloride is used:



The secondary amines are still stronger base formers than the primary amines. They form salts with acids in the same way:



No free nitrogen is liberated when they are treated with nitrous acid, but instead, compounds called nitrosamines are formed:



**Tertiary Amines.**—All three of the hydrogens of ammonia may be replaced by alkyl radicals, forming compounds called tertiary amines. They may be pre-



pared by a method similar to that for primary and secondary amines:

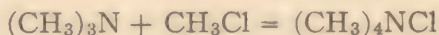


As a matter of fact, the product of such a reaction is a mixture of primary, secondary, and tertiary amines. The relative amounts of the three that are formed depend on the proportions in which the reagents are used. The tertiary amines form salts with acids just as the primary and secondary amines do. They do not react with nitrous acid.

**Tetra-Alkyl Ammonium Compounds.**—A further interesting reaction of the amines, in which their resemblance to ammonia is particularly striking, may be illustrated by the use of trimethylamine  $(\text{CH}_3)_3\text{N}$ . When ammonia is treated with hydrochloric acid, an addition compound is formed:



A similar reaction occurs when trimethyl amine is treated with methyl chloride:



The product is called tetramethyl ammonium chloride. Ammonium chloride is considered to be a salt of the base ammonium hydroxide,  $\text{NH}_4\text{OH}$ . This base is supposed to be formed by the addition of water to ammonia when that compound goes into solution. It is so unstable, however, that it exists only in solution, and decomposes when attempts are made to separate it.

In the same way, tetramethyl ammonium chloride is considered to be a salt of the base tetramethyl ammonium hydroxide  $(\text{CH}_3)_4\text{NOH}$ . This compound is much more stable than ammonium hydroxide, and may be prepared by treating the chloride with silver hydroxide:



Tetramethyl ammonium hydroxide is a colorless crystalline solid. It is a very strong base, comparable with sodium or potassium hydroxides. Its formation and its similarity to ammonium compounds furnish excellent indirect evidence for the existence of ammonium hydroxide.

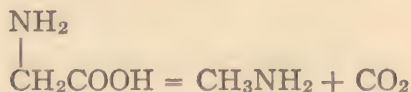
Certain amines are formed during the putrefaction of proteins and some of these are very toxic. They will be mentioned again in a later chapter. The alkaloids are very complex amines which are formed principally in plants, and are of especial interest because of their value in medicine. In general, however, the amines themselves are of rather slight physiological importance.

**Amino Acids.**—A group of compounds which are both primary amines and acids is of the greatest importance, because these compounds are the units of which the complex proteins are composed. The simplest compound of this kind is glycocoll, or amino acetic acid,  $\text{NH}_2\text{CH}_2\text{COOH}$ . Due to its carboxyl group, this compound is an acid which may form salts with metals and esters with alcohols. Due to its amine group it resembles ammonia in being a base

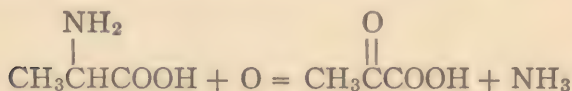
former. It forms salts with acids, and also amides with organic acids. Such compounds are called amino acids.

**Chemical Properties.**—There are three types of reactions that the amino acids undergo that are of especial interest because they take place in the animal body.

The removal of the carboxyl group is brought about by the action of certain bacteria in the intestinal tract. This change is similar to the preparation of methane from sodium acetate by heating it with sodium hydroxide. The essential feature of this preparation is the removal of carbon dioxide from the acid, leaving the hydrocarbon. In the case of amino acids, carbon dioxide is removed, leaving the corresponding amine. With glycocoll the reaction is as follows:



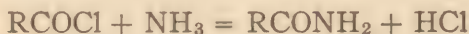
The removal of the amine group from amino acids takes place in the liver and perhaps other organs of the body, and in the intestine due to the action of bacteria. This change is brought about principally by the partial oxidation of the amino acids, forming ammonia and the corresponding ketone acid. With alanine the reaction is as follows:



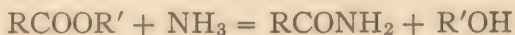
A third type of reaction of the amino acids will be discussed in the paragraph on the peptids.

**Acid Amides.**—The acid amides have been mentioned several times. They contain the  $\text{—NH}_2$  group as the amines do, but differ considerably from the latter in their properties. They may be considered as derived from organic acids by replacing the acid hydroxyl group by  $\text{—NH}_2$ . Thus they bear the same relation to amines as acids do to alcohols, or as acid chlorides do to the chlorine substitution products.

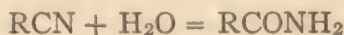
The acid amides may be prepared by treating acid chlorides with ammonia:



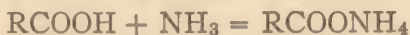
or by the action of ammonia on esters:



As has been stated, they are the first products of the action of water on alkyl cyanides:



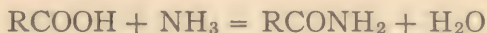
In the presence of sufficiently strong dehydrating agents, acid amides are formed by the direct action of ammonia on organic acids. The ammonium salt of the acid is formed first:



This then loses a molecule of water, forming the acid amide:

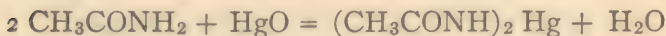


For convenience these two equations may be combined :

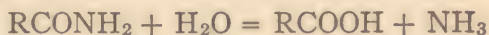


This appears to be the method of formation of acid amides in living organisms.

**Properties.**—The properties of the  $\text{—NH}_2$  group in the acid amides seem to be affected by the neighboring carbonyl group. In these compounds the  $\text{—NH}_2$  group is only very slightly basic in character. It has only a slight tendency to form salts with acids and such salts as are formed are quite unstable. On the other hand, the hydrogens of the  $\text{—NH}_2$  group are slightly acid in character, forming salts with certain metals. Thus mercuric oxide is dissolved by acetamide with the formation of a salt:



In general the acid amides are rather stable and inactive compounds. They are hydrolyzed fairly easily with the formation of the corresponding acid and ammonia:



**Urea.**—The amides of the acids of the fatty acid series are not of great physiological interest, but several other amides are quite important. Urea may be considered as formed by the dehydration of ammonium carbonate, just as acetamide is formed by the loss of water from ammonium acetate:





It is, then, the diamide of carbonic acid. It is the form in which most of the waste nitrogen is excreted from the bodies of the higher animals.

**Asparagine and Glutamine.**—The amides of two amino acids are quite widely distributed in plants.

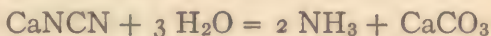
These are asparagine,  $\begin{array}{c} \text{CHNH}_2\text{COOH} \\ | \\ \text{CH}_2\text{CONH}_2 \end{array}$ , the mono-amide of the dibasic acid aspartic acid,  $\begin{array}{c} \text{CHNH}_2\text{COOH} \\ | \\ \text{CH}_2\text{COOH} \end{array}$ , and glutamine,  $\begin{array}{c} \text{CHNH}_2\text{COOH} \\ | \\ \text{CH}_2\text{CONH}_2 \\ | \\ \text{CH}_2\text{COOH} \end{array}$ , the mono-amide of glutamic acid,  $\begin{array}{c} \text{CHNH}_2\text{COOH} \\ | \\ \text{CH}_2\text{COOH} \end{array}$ .

These compounds seem to serve somewhat the same function in plants as urea does in animals. They are not excreted, but under suitable conditions are used again for the synthesis of new plant substances. Thus they serve as a form of temporary storage for nitrogen.

**Cyanamide.**—An interesting compound of this group is cyanamide,  $\text{NH}_2\text{CN}$ , which is the amide of cyanic acid,  $\text{HOCN}$ . The hydrogens of the  $-\text{NH}_2$  group of this amide are distinctly acid. The calcium salt is prepared on a large scale by heating calcium carbide in an atmosphere of nitrogen:



The product, calcium cyanamide, is used to a considerable extent as a source of nitrogen in fertilizers. When treated with water it is decomposed slowly, and ammonia is formed:

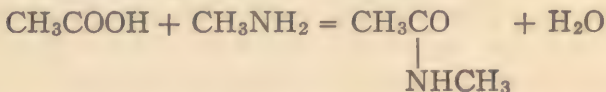


This reaction is the basis for one of the commercial methods for the manufacture of ammonia.

**Substituted Acid Amides.**—One of the methods given for the preparation of acid amides is by the direct action of ammonia on an organic acid. The formation of acetamide would be represented as follows:

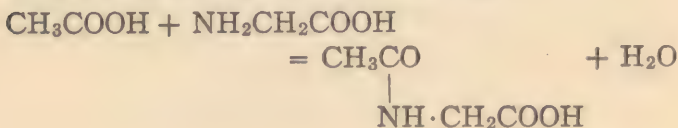


It has been stated that the amines, or substituted ammonias, resemble ammonia very closely in many of their properties. One of these resemblances is in their action on organic acids. Thus methyl amine reacts with acetic acid just as ammonia does:



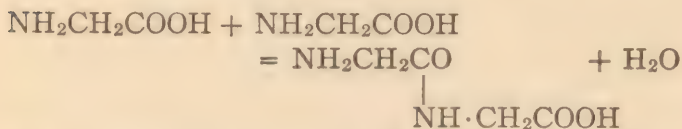
The product of this reaction is a substituted amide, monomethyl acetamide.

The amine group of the amino acids acts in the same way as the  $\text{—NH}_2$  group of the amines. Thus glycocoll reacts with acetic acid as follows:



forming another substituted acid amide, which is called acetyl glycine.

**Peptides.**—In the same way two molecules of glycoll, or glycine, may react with each other, the amine group of one molecule reacting with the acid —OH of the other:



The product is a substituted acid amide of glycoll, called glycyl glycine. Compounds formed in this way are called peptides, and it is in this form of union that the parts of the protein molecule are combined with each other. This is the third and the most important of the types of reactions that the amino acids undergo in living organisms. The other two types were mentioned in a previous paragraph.

When heated with dilute acids, the peptides are resolved by hydrolysis into their constituent amino acids. The above reaction is a reversible one. The direction in which it proceeds depends on the conditions to which the mixture is subjected. Going to the right, it is a condensation reaction; to the left, one of hydrolysis.

## CHAPTER XI

### THE PROTEINS

The proteins form the third, the most complex, and in many ways the most important of the groups of food substances. A very large number of different proteins is known. They comprise the larger part of the solids of animal bodies, but a much smaller proportion of the dry weight of plants, since the carbohydrates predominate in plants. A large part of the solids of the white of eggs consists of a protein called egg albumin. Milk contains at least two proteins, lactalbumin, which forms a scum on the surface of milk when it is heated, and casein, which forms the curd when milk sours. In plants, proteins are most abundant in certain seeds. Those of the legumes, such as peas, beans, and soy beans are especially high in protein. Seeds that are rich in oil often contain large amounts of protein. Thus the press cake left after removing the oil from flaxseed and cottonseed is valuable as a feed because of its high protein content.

Proteins are present wherever there is life, and they seem to be the substances most intimately associated with living matter. They do not occur pure, but

several different ones are usually found together, and mixed with many nonprotein substances. They are all amorphous colloidal substances, and they differ quite widely in solubility and in some other properties.

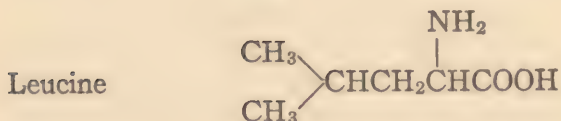
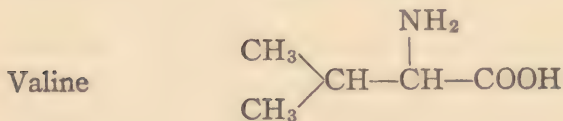
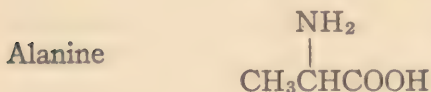
**Composition.**—The proteins all contain the elements carbon, hydrogen, oxygen, and nitrogen. Most of them contain sulfur, and many of them phosphorus. Beside these, small amounts of other elements, such as iron and calcium, are often found combined with the proteins. The proteins differ considerably in the relative amounts of these elements they contain, but their average elementary composition may be given about as follows: carbon, 50 per cent; hydrogen, 7 per cent; nitrogen, 16 per cent; oxygen, 25 per cent; sulfur, 0.3 per cent; phosphorus, 0.3 per cent. There is no exact knowledge of the molecular weight of the proteins, but it is undoubtedly very large. It is very difficult to prepare proteins in anything like a pure condition, and therefore determinations of their molecular weight are likely to be far from accurate. Some estimates have been made, and these place the molecular weight of egg albumin at about 15,000, and that of some of the other proteins at similar values.

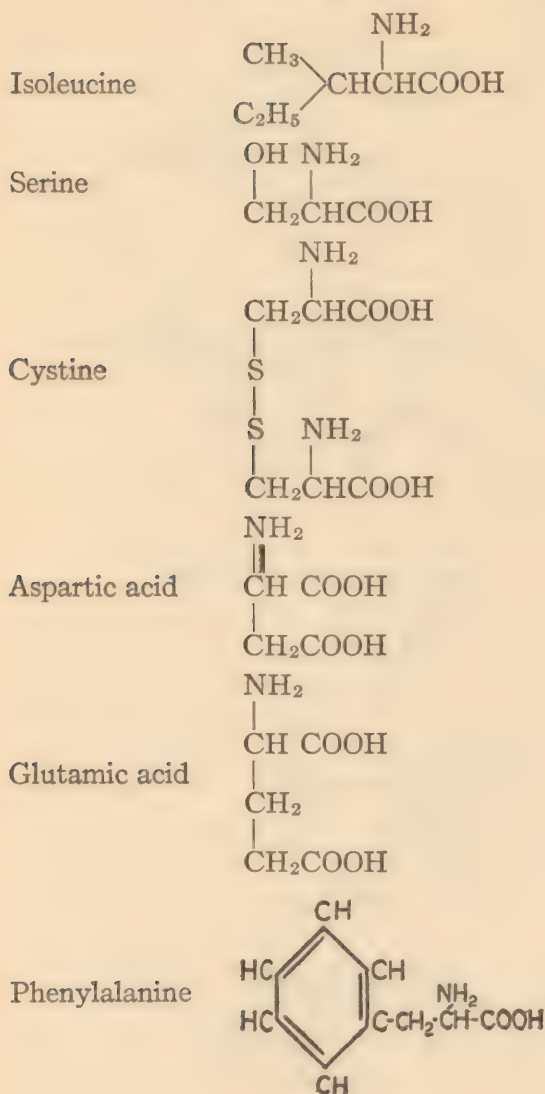
Of course the elementary composition of the proteins furnishes no clue to their structure, or to the nature of the chemical groups of which they are composed. In the case of the complex carbohydrates, this information was obtained by a study of the products of their hydrolysis. Thus starch is considered to be composed of a number of glucose molecules combined



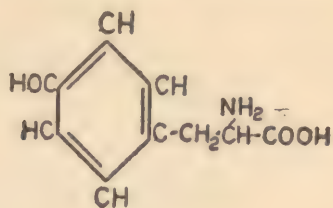
with each other with the loss of water because, on hydrolysis, water is added and glucose is formed. The hydrolysis of the proteins may be effected by the aid of acids, of alkalis, or of catalytic agents formed by living organisms. In all cases the products formed are essentially the same. The elements of water are added and a mixture of amino acids is produced. It is concluded, then, that the protein molecule is composed of a large number of amino acid molecules combined with each other with the loss of a corresponding number of molecules of water. The amino acids are combined with each other in the way just described for the peptides, that is, as substituted acid amides.

**The Constituent Amino Acids.**—The following seventeen amino acids have been separated from the products of hydrolysis of the proteins:

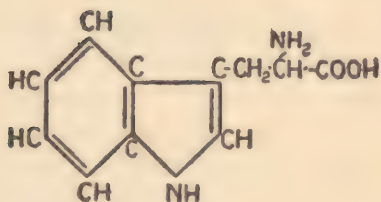




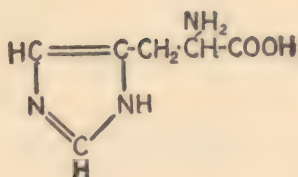
Tyrosine



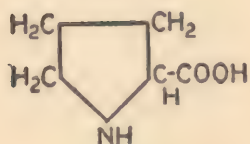
Tryptophane



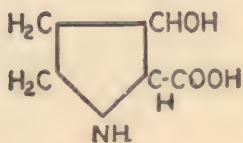
Histidine

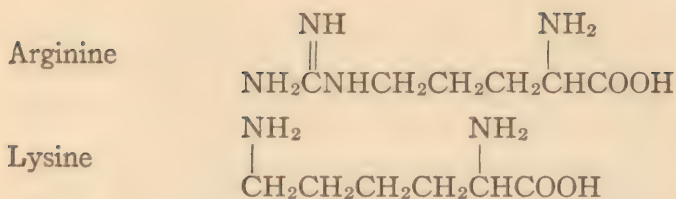


Proline



Oxyproline





Since the separation of certain of these acids is very difficult, it is possible that small amounts of still others occur.

The relative amounts of the different acids vary widely in different proteins. Thus gliadin, one of the proteins of wheat flour, contains 40 per cent of glutamic acid, and the globin of the blood contains only 2 per cent of this acid. Some of the amino acids are entirely lacking in certain of the proteins. Gelatin, which is prepared by steaming bones, contains practically no tryptophane, tyrosine, or cystine; and zein, a protein found in corn, lacks both lysine and tryptophane. The amino acid content of proteins is an important factor in their value as foods.

**Definition and Number.**—The proteins may be defined as complex organic compounds which yield amino acids on hydrolysis. Since so many different amino acids may take part in the formation of the protein molecule, and since the proteins differ widely in the relative amounts of the different amino acids they contain, it is evident that the possibilities for the existence of different proteins are practically limitless. It will be noted also that, with the exception of glyco-coll, all the amino acids in the list just given contain an asymmetric carbon atom, and so each of them may

exist in two forms. This of course adds countless more possibilities of different proteins to those due to different proportions and arrangements of the amino acids in the protein molecule.

**General Properties.**—It is not surprising that the proteins should differ quite widely in many of their properties. In certain ways, however, they are all much alike. They are all colloidal substances, which are able to absorb or imbibe greater or smaller amounts of water. This property is of the greatest importance, since it aids in controlling the physical consistency of the protoplasm and of other parts of organisms which are composed largely of proteins. This power of absorbing water is affected to a remarkable degree by certain changes in the nature of the solution with which the proteins are in contact. One of these factors is the reaction of the solution. Most proteins absorb the least water from solutions that are nearly neutral, and much more from solutions that are slightly acid or alkaline. The kind and amount of inorganic salts present in the solution also have important effects on the amount of water imbibed.

**The Formation of Salts.**—The other general properties of the proteins may be discussed best in connection with those which are soluble. In forming the protein molecule, most of the amine and carboxyl groups of the amino acids combine with each other in the manner that has been described, and thus are rendered inactive. A few of both groups always remain free, and thus the protein itself is both an acid and a base, able to form salts with both bases and acids. This is



undoubtedly the principal reason for the remarkable effect of the reaction of the solution on the water absorbing power of the proteins. For instance, in dilute sodium hydroxide, sodium proteinate would be formed. The dissociation of this salt would give the protein a negative charge, since the protein forms the anion of this salt. Conversely, in a solution of hydrochloric acid protein chloride would be formed. As the protein forms the cation of this salt, its dissociation would give the protein a positive charge. In a neutral solution protein is only very slightly dissociated, and so carries practically no charge. The sign of the charge on an ion or particle influences its properties very greatly.

With certain acids and certain bases the proteins form salts which are insoluble. These reagents may be used to precipitate the proteins, and are very important helps in the study of these substances in the laboratory. Among the acids most commonly used for this purpose are tannic acid, phosphotungstic acid, and picric acid. Some of the metals whose protein salts are more or less insoluble are copper, lead, and mercury.

**Salting Out.**—It will be remembered that it is possible to “salt out” soaps by adding fairly large amounts of sodium chloride to their solutions. In the same way, high concentrations of certain salts precipitate proteins from their solutions. This is a method that is used very often in the laboratory, since it precipitates the protein unchanged, and also is useful in separating certain proteins from mixtures. The salts

used most frequently for this purpose are ammonium sulfate, zinc sulfate, and sodium chloride.

**Coagulation.**—Most proteins are insoluble in fairly concentrated solutions of alcohol. This furnishes another method for their precipitation. If the precipitated protein remains in contact with the alcohol for some time, a peculiar change occurs and the protein is no longer soluble in water; it is said to be coagulated. The same change occurs on heating the solution of a protein, as is illustrated by the change in the white of an egg on cooking. Proteins coagulate most readily at a rather definite degree of acidity, quite near the neutral point, where both the acid and basic properties of the protein are least pronounced. Coagulation occurs in two steps: first there is a change, perhaps both chemical and physical, which brings the protein into the form of something like an extremely fine suspension; the particles of protein then flocculate and settle out of the solution. The second step requires the presence of certain electrolytes; if these are not present, the first step may take place without the second, and the protein is said to be "denatured." Insoluble proteins also may undergo such a change. It is quite probable that the loss of vitality in seeds is due to a gradual denaturing of the proteins in their embryos.

**Hydrolysis.**—Proteins differ widely in the ease with which they are hydrolyzed by acids. In general they are much more resistant than the storage carbohydrates, and their complete hydrolysis requires long continued boiling with moderately concentrated acids.

Like the hydrolysis of starch, that of proteins is a gradual change, and several intermediate products are formed between the proteins and the amino acids of which they are composed. Among these intermediate products are the proteoses, peptones, and peptides, which will be mentioned again in the classification of the proteins.

Proteins also are hydrolyzed by the aid of catalysts secreted by living cells. These catalysts act on the proteins of food during the process of digestion, and convert them into their constituent amino acids. Part of the amino acids resulting from the hydrolysis of the food proteins are combined again, or condensed, to form the proteins used in building the body tissue. Thus the proteins, like the fats and carbohydrates, are formed by the condensation of the simple units of which they are composed, and on hydrolysis they are decomposed again into these units.

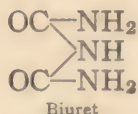
**Color Tests.**—There are no reactions sufficiently characteristic of the protein molecule as a whole to be used as qualitative tests for the presence of these substances. There are, however, certain color reactions that are given by chemical groups which are usually present in the protein molecule, and often these are used to detect the presence of proteins.

**The Xanthoproteic Reaction.**—On treating a protein with concentrated nitric acid, a brilliant yellow color is produced. If the mixture is made alkaline with ammonium hydroxide, the color changes to a deep orange. This reaction is familiar to any one who has had nitric acid on his fingers. The reaction is

given by the proteins of which the skin is composed. The color is due to the action of the nitric acid on the benzene rings present in such amino acids as phenylalanine and tyrosine. The colored product is very similar to picric acid.

**Millon's Reaction.**—A red color develops when a protein is heated with a solution of mercuric nitrate containing a little mercuric nitrite. Tyrosine is responsible for the development of this color, and proteins which do not contain this acid do not give this test.

**The Biuret Reaction.**—If a very dilute solution of copper sulfate is added to a strongly alkaline solution of a protein, a color is produced ranging from violet to pink, according to the nature of the protein present. The color is due to a certain combination of peptid linkings. The test is used in following the course of the hydrolysis of proteins. The name, biuret, is that of a simpler compound which gives the test:



This compound may be considered as formed from two molecules of urea by the loss of a molecule of ammonia.

**The Hopkins-Cole Reaction.**—A solution of protein mixed with a solution containing glyoxylic acid,  $\text{COOH}$ , is stratified on concentrated sulfuric acid.





At the zone of contact, a violet ring is formed. The color is due to the presence of the amino acid tryptophane in the protein molecule.

**Quantitative Determination.**—For routine analyses of feeding stuffs and for many other purposes, the total amount of protein present in a sample is estimated by multiplying the total nitrogen present by 6.25. This factor is used because the average nitrogen content of proteins is 16 per cent. The method is inaccurate for two reasons: not all proteins contain exactly 16 per cent of nitrogen; and often not all the nitrogen in a sample is present in the form of proteins. However, the method is sufficiently accurate for many purposes. A direct determination of the amount of protein present in a sample is impossible, in many cases, because of the variation in solubility of the proteins and the difficulty of separating them from other substances.

**Classification.**—Due to the very incomplete knowledge of the proteins, an entirely satisfactory classification of them is impossible. The best classification that has been made is based in part on differences in solubility and in part on differences in composition. This classification follows, together with some examples of each of the groups.

I. *The Simple Proteins* do not appear to be combined with any nonprotein substances. The subdivisions are based on solubility.

A. *Albumins* are soluble in water and are coagulated by heat. They are widely distributed in both animals and plants, but are usually present in com-



paratively small amounts. Egg albumin is the best known member of this group.

B. *Globulins* are insoluble in water but are dissolved by dilute salt solutions. They may be precipitated from these solutions by dilution or by removal of the salts by dialysis. They are coagulated by heat. Globulins often occur along with the albumins and frequently in larger amounts than the latter. They have been separated from many seeds. One of the most carefully studied of these substances is Edestin, which is found in hempseed. A globulin also occurs in the blood.

C. *Glutelins* are insoluble in water or dilute salt solutions, but are dissolved by dilute acids or alkalis. The best known member of this group is glutenin, which is one of the proteins comprising the gluten of wheat flour.

D. *Prolamines* are not soluble in any of the solvents mentioned, but have the property, very unusual in the proteins, of dissolving in 70-90 per cent alcohol. In more dilute or more concentrated alcohol they are insoluble. Gliadin of wheat flour is an example. Glutenin and gliadin together comprise the gluten of flour. The peculiar sticky tenacious properties of this mixture enable it, when wet, to entangle bubbles of gases, which expand on heating thus forming a light dough. Wheat and rye seem to be the only cereals containing proteins of the right character and amount to make a light dough.

E. *Albuminoids* are insoluble and in general very resistant to hydrolysis. They occur in the connective

and protective tissues of animal bodies. Collagen occurs in bones and cartilage. When these are steamed, partial hydrolysis occurs and glue is formed and, by further refining, gelatin is produced. Keratin occurs in hoofs, horns, hair, feathers, and skin. It is very resistant to the action of chemicals and so forms excellent protective coverings. Elastin is found in the yellow elastic fibers of ligaments and in the walls of arteries. It is more easily hydrolyzed than collagen or keratin.

II. *The Conjugated Proteins* are compounds of simple proteins with some nonprotein group. They are subdivided according to the nature of the nonprotein group, which is usually acid.

A. *Chromoproteins* contain a colored nonprotein group. Examples are the hemoglobin of the blood and certain colored substances in plants, such as phycoerythrin, to which the color of certain algae is due.

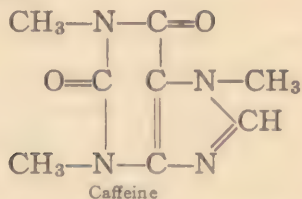
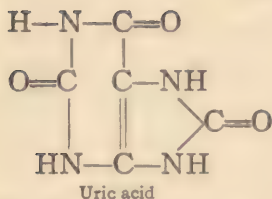
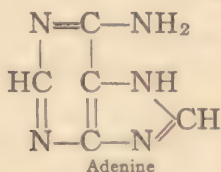
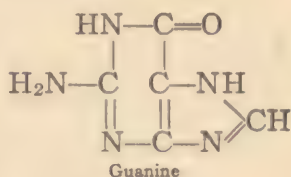
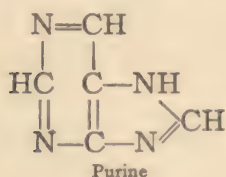
B. *Glycoproteins* contain a carbohydrate in the non-protein group. The mucin which gives the peculiar stringy character to saliva is an example.

C. *Phosphoproteins* are composed of simple proteins combined with phosphoric acid and probably some other unknown substance. Casein, the principal protein of milk, is a member of this group.

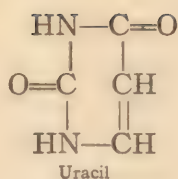
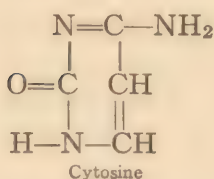
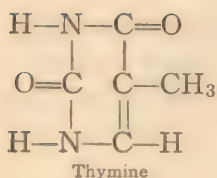
D. *Nucleoproteins* are very complex substances which are important constituents of the nuclei of cells. The first products of their hydrolysis are a protein and a substance called nuclein. Nuclein is decomposed

by further hydrolysis into another protein fraction and nucleic acid.

The products of hydrolysis of nucleic acid are a sugar, phosphoric acid, and two groups of nitrogen containing compounds, the purine bases and the pyrimidine bases. The purine bases combined in the nucleoproteins are adenine and guanine, which are regarded as derivatives of purine. Caffeine, the active principle of coffee and tea, and uric acid, one of the forms in which nitrogen is excreted from the human body, are also purine derivatives.



The pyrimidine bases found among the products of hydrolysis of the nucleic acids are thymine, cytosine, and uracil.



III. *The Derived Proteins* constitute an artificial group, including the various decomposition products of the naturally occurring proteins. They may be produced by physical agencies, such as heat, by chemical agents, or by catalytic agents produced by living organisms. Synthetic compounds resembling the proteins also are included. Subdivisions are based partly on the degree of decomposition and partly on solubility.

A. *Primary Derivatives* are the products of only slight changes in the naturally occurring proteins.

1. *Coagulated Proteins* are the insoluble products of the action of heat or alcohol on the proteins.

2. *Metaproteins* are among the first products of the action of acids or alkalies on proteins. They are soluble in dilute acids or alkalies, but insoluble in neutral solutions.

B. *Secondary Derivatives* are products of the hydrolysis of proteins intermediate between the metaproteins and the amino acids. They bear much the same relation to the proteins that dextrins and maltose do to starch.

1. *Proteoses* are soluble in water. They are not coagulated by heat, but are precipitated by saturating their solutions with ammonium sulfate.

2. *Peptones* represent a more advanced stage in the hydrolysis of proteins. Their molecular weight is probably smaller than that of the proteoses, and they are not precipitated by saturating their solution with ammonium sulfate.

3. *Peptides* are compounds of two or more amino acids, whose composition is known. They represent the stage in the hydrolysis of proteins just previous to complete decomposition into the constituent amino acids. Many peptides have been synthesized and some of them are quite complex. Emil Fischer succeeded in preparing a peptide containing eighteen amino acid molecules, whose molecular weight is about 1,200. This peptide has the properties of a proteose.



## CHAPTER XII

### THE GENERAL CHEMISTRY OF LIVING ORGANISMS

Many organisms, such as amoebae, yeasts, and bacteria, are composed of single cells. All their functions as living beings, then, must be connected with this simple structure. These cells may contain granules of various substances, such as the food particles ingested by amoebae, and oil drops. Most single celled organisms also form protective coverings around themselves. The phenomena of life, however, are not associated with any of these structures, but with the usually clear, semifluid substance within the cell. This substance, protoplasm, is the seat of all the activities of the living cell. It is this substance which moves in response to changes in external conditions; it grows by adding to itself some of the materials contained in its food; it divides itself and forms two new cells; and it oxidizes some of its food, securing the energy used in carrying on these functions.

In more complex organisms, the many cells of which they are composed become differentiated into groups called tissues. The different tissues may vary widely in appearance and structure, in the particular types

of physical and chemical changes that predominate in them, and in the relation they bear to the activities of the organism as a whole. Thus in the human body the activity of muscular tissue is evidenced principally by contraction, that of nervous tissue by irritability, that of glandular tissue by the elaboration of certain secretions.

Yet differing as widely as they do, the cells of these tissues all contain protoplasm which, in its general properties, is much the same in all cases. Movement, growth, and respiration in higher organisms are functions of the protoplasm of individual cells, just as they are in the simplest forms of life. The carrying on of these functions involves constant and rapid changes, both physical and chemical, in the protoplasm. In fact, when these changes cease, life ceases.

**The Composition of Protoplasm.**—Attempts to separate the constituents of protoplasm result in the death of the cell. This involves a decided change from the very active, labile condition which holds in living protoplasm to the much more stable and less active condition of dead matter. Thus the means for studying the nature of living protoplasm are limited and indirect. Chemically, protoplasm is composed of a mixture of fats, carbohydrates, and proteins in varying amounts, together with other related substances, all dissolved or suspended in a very large amount of water. Mineral elements are always present, partly combined with the organic molecules and partly in the form of inorganic salts. These organic substances in protoplasm are being broken down constantly into

simpler waste products in the course of the activity of cells, and their place is taken by materials used as food. If more food is obtained than is necessary to repair the waste, the excess may be accumulated, or used in growth.

**The Physical Nature of Protoplasm.**—Protoplasm is a liquid, but its viscosity differs widely in different cells, and in the same cell at different times. Many of the constituents of protoplasm are present in the colloidal condition. The brief discussion of this condition which follows may give some idea of the physical nature of protoplasm, and its importance in the life of the cell.

**Suspensions.**—If a sample of clay or some other insoluble substance in a very finely divided condition is shaken with water, it will be noted that the larger particles separate first. The finest particles may stay in suspension for a long time, hours or even days. The rate of settling is roughly proportional to the size of the particles. The smaller a particle is, the greater its surface compared with its mass. Its fall is hindered by the resistance, or friction, due to the viscosity of the water, which acts on the surface of the particle. The effect of gravity, which makes the particle settle, is proportional to its mass. Thus, when the relation of surface to mass increases, the rate of fall decreases. By suitable means it is possible to obtain particles so small that they do not settle at all, that is, their weight is not sufficient to overcome the viscosity of water acting on their surface. The particles in suspension are charged electrically, and all the particles of the

same kind carry charges of the same sign. These charges tend to keep the particles from coming together, or flocculating, as they will do when the charges are neutralized. Small particles in suspension have an irregular vibratory motion, called Brownian movement, which is more pronounced the smaller the particle. This aids in keeping the particles in suspension.

**Suspension Colloids.**—A very considerable difference in size exists between particles of molecular dimensions and those large enough so that they just do not settle. Especially the more finely divided particles in this range give suspensions which appear very much like true solutions. However, their properties show that the particles and the water in which they are suspended are distinct, whereas true solutions are homogeneous. Such mixtures form one group of the so-called "Colloidal Solutions." They are called suspension colloids because they seem to consist of solid particles suspended in a liquid. Metals that do not react with water, and insoluble salts usually are obtained easily in the colloidal condition. Salts that are soluble in water often may be suspended (or dispersed) in other liquids in which they are insoluble.

It is found that these suspension colloids are charged electrically, positively or negatively according to the nature of the substance. If an electrolyte, acid, base, or salt, is added to a suspension colloid, the particles come together, or flocculate, and settle. This probably is due to the neutralization of the charge on the colloid particles by the ion of the electrolyte having a charge of the opposite sign.



Colloidal gold, which is negative, is precipitated by a certain concentration of  $\text{NaCl}$ , but by a much smaller concentration of  $\text{CaCl}_2$ ; and still less  $\text{FeCl}_3$  is required. The precipitation is due to the neutralization of the negative charge on the gold particles by the positively charged ion of the salt, and  $\text{Ca}^{++}$ , being divalent, is much more effective than the monovalent  $\text{Na}^+$ ;  $\text{Fe}^{+++}$  is still more effective than  $\text{Ca}^{++}$ . A similar result is obtained when lime is added to a clay suspension. The finely divided negatively charged clay particles come together forming larger particles, due to the effect of the positive calcium ion. This is one of the beneficial effects of adding lime to soils.

On the other hand, colloidal ferric hydroxide is charged positively. It, too, is precipitated by  $\text{NaCl}$ , but due to the negative chlorine ion. It is precipitated by much smaller amounts of  $\text{Na}_2\text{SO}_4$ , due to the divalent negative sulfate ion, and by still smaller amounts of  $\text{Na}_3\text{PO}_4$  because of the trivalent phosphate ion.

**Emulsions.**—Liquids which are insoluble in water also may be dispersed more or less permanently. Such a suspension is called an emulsion. If oil and water are shaken together, the small oil drops formed run together as soon as the shaking is stopped, and the oil separates from the water. In order to keep the suspended drops from running together, it is necessary to add some substance which seems to form a film around the droplets. Soap is used very commonly as an emulsifying agent. In the case of the fat in milk, the protecting substance appears to be a protein.



In general these emulsions are not precipitated by salts as easily as are the suspension colloids, but a salt which makes the emulsifying agent insoluble causes the emulsion to separate. If soap is used to emulsify an oil, the addition of a calcium salt breaks the emulsion, because the calcium salts of the fatty acids of the soap are insoluble, and thus the protecting film is removed from the drops of oil. For this reason it is necessary, in making the oil emulsions used as sprays, to use soft water so that the emulsifying power of the soap is not destroyed.

However, if, to an emulsion of an oil in a soap solution, just the right amount of a calcium salt is added (enough to convert slightly more than half of the soap to the calcium salt) and the mixture is shaken, an emulsion is again obtained. This emulsion differs from the original one in many of its properties. It does not appear as watery as the former one, and the sound produced on shaking it is like that produced by shaking an oil. The original emulsion, when shaken, sounded like water. The new emulsion consists of water suspended in oil, instead of oil suspended in water. The change probably is due to the solubility of the calcium soaps in the oil.

It is evident that since the oil is now on the outside and continuous, and the water is inside and not continuous, the change affects very strikingly the solubility of various substances in the emulsion, and their ability to diffuse through it. For instance, sugar would diffuse readily through the original emulsion, but could not penetrate the new one, since sugar is not soluble

in fats. Changes similar to this may be considered to take place in the protoplasm of a cell under the influence of varying amounts of the different salts present, and they would cause changes in the permeability of the protoplasm.

**Emulsion Colloids.**—The term colloid means glue-like, and there are a great many substances, of which glue is one, that differ considerably in their properties from the suspension colloids just described. The members of this group are called emulsion colloids. From the physiological point of view, they are much the most important of the colloids. Soap and gelatin are members of this group, which also includes many of the complex carbohydrates and most of the proteins. Though these substances differ considerably among themselves, a brief description of the properties of gelatin will give an idea of their general characteristics.

Gelatin is soluble in water, but its solution seems to consist of two parts; one is a dilute solution of gelatin in water, in which is suspended the other part, which may be described best as a solution of water in gelatin. Thus a gelatin solution is not homogeneous, but consists of two parts differing in the relative amounts of water and gelatin they contain. The outer phase, or dispersion medium, is a dilute solution of gelatin in water; the inner, or disperse, phase contains much less water and more gelatin, and is much more nearly solid. Thus the two phases differ from each other, but not nearly as widely as the two phases of a suspension colloid, such as colloidal gold. This is the

condition of the dilute gelatin solution when it is warm. On cooling, a change takes place which is very similar to the one described above as occurring when calcium salts are added to an emulsion of oil. The more nearly solid solution of water in gelatin becomes the outer phase, and in this is dispersed the dilute solution of gelatin in water. When this change in structure occurs, the solution gels, or becomes nearly solid. The structure of the gel seems to be very much like that of a honeycomb, with the dilute gelatin solution filling the compartments whose walls are formed of the part containing less water and more gelatin.

This tendency to form gels is influenced by the presence of certain salts. Some, such as sulfates, make the gel form more readily; others, such as nitrates, hinder the formation of a gel. This is another way in which salts may affect the properties of living protoplasm.

Many proteins, such as egg albumin, do not form jellies readily, but on heating they are coagulated. This coagulum is a sort of a gel in which much less water is included than is held in a gelatin jelly. The coagulation of proteins is favored by the same salts which favor gel formation in gelatin, and is retarded in the same way by nitrates.

**Water Absorption.**—When dry, gelatin is able to absorb large amounts of water without going entirely into solution. As the water is absorbed, or imbibed, the gelatin changes gradually from a hard dry film to a jellylike mass into which soluble substances may diffuse readily. This property of imbibing

water is common to many of the emulsion colloids present in living cells, and it is extremely important in regulating the water relations and the physical consistency of the cell. This imbibition of water is affected to a remarkable degree by other substances present in solution. Acids and alkalies are particularly important in this connection, and this effect differs with different kinds of colloids. Thus gelatin takes up the most water from solutions that are slightly acid, somewhat less from those that are slightly alkaline, and least of all from solutions that are nearly neutral. Agar, which is a colloidal carbohydrate, imbibes enormous amounts of water from neutral solutions, but much less from those that are either acid or alkaline. Since cells are composed of colloids that are similar in their properties to gelatin and agar, it is evident that the reaction of the cell is extremely important in determining its physical condition and its water relations.

**Surface Films.**—There is another property of some of the substances that are present in protoplasm that is of importance. When they are dissolved, it is found that they are more concentrated in the surface of the solution than in its interior. This property is especially marked in the soaps and in related substances. In many cases the surface of the solution becomes almost solid, and has properties very different from those which characterize the interior of the solution. In the cell, such a film is formed wherever the protoplasm is in contact with air, or any substance unlike itself. The surface film formed in this way



acts as a membrane which regulates the amount and kind of material that may enter or leave the cell by diffusion. The effects of salts and of acids and alkalies on this membrane are such as have been noted above. Varying concentrations of inorganic substances, then, are able to regulate the physical condition of the cell membrane and through this its permeability.

**Food.**—The activities of cells are supported by materials that reach them from their surroundings. The materials used are of the same general nature as the cell itself, that is, fats, carbohydrates, proteins, water, and mineral salts. All these substances that may repair waste or provide the raw materials for growth may be called foods. The organic substances actually used by cells are relatively simple, such as glucose and the amino acids, but the foods themselves, such as starch, fats, and proteins are very complex and many of them are insoluble.

**Digestion.**—Before being used by the cells, these complex substances are decomposed into their simpler components by hydrolysis. Starch is converted into glucose, fats into glycerol and fatty acids, and proteins into their constituent amino acids. This process of preparing foods for absorption by the cell is called digestion. It is an hydrolytic process. In general the complex insoluble foods are changed by hydrolysis to their simpler soluble components. These hydrolytic changes are hastened by catalytic agents secreted by the cells. The action of these catalysts may take place in the cells which secrete them, as is true in the case of amoebae and in certain of the storage organs of



plants; or the catalysts may act on substances outside the cell, as occurs with many bacteria and the higher animals.

**Metabolism.**—After digestion and absorption, the food substances may be used in several different ways. All the changes these compounds undergo from the time they are absorbed by the cells until the waste products to which they give rise are formed, are grouped under the general term, metabolism. Two types of metabolism may be distinguished: one includes those changes which are synthetic, resulting in the formation of complex substances, protoplasm or complex nonliving structures; these processes are called anabolism. Changes resulting in the breaking down of complex substances and the formation from them of waste products, are grouped under the name catabolism. The latter should not be confused with digestion. Although both are processes of decomposition, digestion results in the formation of compounds which may be used by cells, which are, in fact, the starting point of metabolism; but catabolism results in the formation of waste products, in general not capable of being used by the cell, which are the final products of metabolism.

**Anabolism.**—The results of the anabolic, or synthetic, activities of cells depend in part on the type of cell, and in part on the amount of food available. The activities of cells result in the destruction of part of their own substance. This waste is repaired by the building up of these complex parts from the simpler compounds of the food. Fats may be formed by the

combination of fatty acids with glycerol; complex carbohydrates by the combination of simple sugars; and proteins by the combination of amino acids. These are all condensation reactions, the combination of two or more molecules with the loss of water.

From the principle of chemical equilibrium, it is evident that the more of these simple products of digestion there are in a cell, the greater will be the tendency for these condensation reactions to proceed. If large amounts of food are available, not only will the waste of the cell be repaired, but new protoplasm may be formed and growth result.

Many nonliving substances also may be formed by the condensation of the products of digestion of foods. In many organisms connective, protective, and supporting structures are formed. Among these are the cell walls of plants, which may consist of pectic compounds, cellulose, or lignocellulose, and the protective and connective tissues of animals, which consist principally of proteins.

In many cases, too, the foods are converted, in part, into complex substances which are stored for a longer or shorter time, and may be redigested and used as food again later; storage of fats, starch and other carbohydrates, and proteins in the seeds of plants is an example. Storage also occurs in roots and stems of biennial and perennial plants, and temporarily in leaves. In animal bodies there is a temporary storage of carbohydrates in the form of glycogen, and a more permanent storage of fats.

Thus the most important type of reaction involved

in maintenance, growth, storage, and the formation of protective and connective structures, is condensation. The products of the hydrolytic process of digestion are recombined forming the complex substances characteristic of the organism.

**Reduction.**—Among the synthetic changes going on in living organisms, certain very important ones are reductions. The reactions of hydrolysis and condensation that have been mentioned involve very little energy change. Reduction reactions require large amounts of energy which is rendered potential in the reduced compounds, and may be liberated again when these compounds are oxidized.

One of the most striking of these reduction reactions is the change of carbohydrates to fats. Reference to the chemical formulas for these two groups of compounds will show that the latter contain much less oxygen in proportion to carbon and hydrogen than do the former. Also the heat of combustion of the fats is much greater than that of the carbohydrates. The change of carbohydrates to fats, then, is a reduction, and uses energy. The most important reduction reaction is the formation of carbohydrates from water and carbon dioxide, which is limited to green plants. This most interesting change will be discussed in a later chapter.

**Catabolism.**—It is undoubtedly true that the wearing out of protoplasm is essentially an oxidation process, and that this is preceded by the hydrolysis of the complex protoplasmic constituents, forming their simpler components, which then are oxidized. It is

probable, too, that some of the food materials are oxidized directly without first being built up into protoplasm.

**Oxidation.**—As has been mentioned, living matter is constantly undergoing changes, both physical and chemical. Energy is required to bring about many of these changes. Thus energy is used in reduction reactions, in any physical changes that result in increased surface, in raising the temperature of the cell, and in movement. This energy is supplied by the oxidation of organic compounds in much the same way that heat may be obtained by burning wood.

Oxidation, then, is one of the most important types of reactions that go on in living organisms, since by this means the energy is supplied without which life is impossible. Normally, the final products of the oxidation of carbohydrates and fats in living cells are carbon dioxide and water. Since these are the same products obtained by burning these compounds, the heat liberated by burning them in air or oxygen is a measure of the energy the cell may obtain from their oxidation.

**Heat Units.**—The unit used in measuring heat is the calorie, which is the amount of heat required to raise the temperature of 1 gram of water 1°. As this differs slightly at different temperatures, the change from 15° to 16° is taken as the standard. For temperatures not far removed from this, the difference is very slight, so that in ordinary work no correction need be made. For measuring food values, the calorie is too small a unit for conveni-



ence, so the Calorie is used, which equals 1,000 of the smaller units. It is written and abbreviated with a capital C. A still larger unit called the Therm also is used, which is equal to 1,000 Calories or 1,000,000 calories.

The heats of combustion of foods are usually stated as the number of Calories of heat liberated when one gram of the substance is oxidized. Thus one gram of glucose yields 4 Calories. Fats differ somewhat in composition and in fuel value, but their average heat of combustion is 9.4 Cal. per gram. When proteins are oxidized in the cell, not all their carbon and hydrogen are changed to carbon dioxide and water, but part remains combined with nitrogen in the form of urea, which is a waste product not capable of further oxidation in the cell. Thus, when burned in the air, proteins yield somewhat more energy than they do when oxidized in the cell.

There are, then, two sets of opposing reactions which include the most important of the chemical changes that go on in living cells. These are oxidation and reduction, hydrolysis and condensation. All these reactions may go on at the same time in the same cell. Just how the cell is organized to make possible the orderly carrying on of such a variety of processes, is not known. If the cell is broken up, the reactions may continue, but no longer in an orderly way; and this lack of coördination soon causes the death of the protoplasm.

**Minerals.**—Many of the mineral elements found in living organisms are absolutely essential. Those



most commonly met are K, Na, Ca, Mg, Fe, S, P, Cl. All of these seem to be essential to the higher animals, but plants appear to be able to grow normally without Na or Cl, and some of the lower plants can grow in a medium free from Ca. Beside those mentioned, the following elements are frequently present in living organisms: Si, F, I, Al, Mn. The mineral elements are present combined with each other in the form of salts, or with C, H, N, and O in the form of organic compounds. They serve two principal types of functions, physical and chemical.

**Chemical Functions.**—Certain mineral elements are constituents of essential organic compounds. Sulfur and phosphorus are present in proteins; iron in the hemoglobin of the blood; calcium, combined with pectic acid, in the cell walls of plants; and magnesium in chlorophyll, the green coloring matter of plants. Aside from this, some of these elements seem to form compounds which exist only for a short time, but which are essential to the changes going on in the food substances. Thus it is supposed that potassium, through some compound it forms with carbohydrates, is an important aid in the synthesis and translocation of these substances in plants.

**Physical Functions.**—Some of the physical functions of the mineral elements have been indicated in the discussion of colloids. Salts play a very important part in regulating the physical condition, the water absorbing capacity, and thus the permeability of protoplasm. This is done by the direct effect of the salts themselves, as is illustrated by the opposing action of

sodium and calcium on emulsions, and by their effect on the flocculation of colloids. An indirect effect also is produced by their influence on the acidity or alkalinity of the medium in which the protoplasm lives. Salts of strong bases and weak acids, or of strong acids and weak bases, are effective in preventing rapid changes in acidity or alkalinity, which would be very injurious. Phosphates and carbonates are especially effective in this respect.

**Water.**—The most abundant and in many ways the most important constituent of living organisms is water. It is the only medium in which life exists. Plants and animals living on dry land are as truly in a watery medium as are fish and other aquatic forms, since their individual cells are composed very largely of water and are incapable of active existence otherwise. Water is the medium in which the colloids forming the protoplasm are dispersed. It is the solvent by means of which food is transported to the cells, and waste products are eliminated. These changes occur according to the principle of diffusion.

**Diffusion.**—If pure water is poured on some crystals of a soluble substance, such as copper sulfate, and the mixture is allowed to stand, in the course of time the salt will be found to be uniformly distributed throughout the solution. While any of the solid salt remains, the solution in contact with it is more concentrated than that farther away. This inequality is overcome by the movement, or diffusion, of the salt from the place of higher concentration to that of lower concentration. This diffusion continues until the salt

is uniformly distributed. There is another feature of this process which should not be overlooked. Where the copper sulfate is most concentrated, the water is least so, and where there is the least of the salt, the concentration of the water is highest. Uniformity of concentration of the solution is reached not only by the diffusion of the salt from the place of high concentration to that of lower concentration, but also by the movement of water from the place where it is most concentrated to that where it is least concentrated. Thus both solute and solvent move, but in opposite directions.

Suppose that by some means copper sulfate is removed from one portion of its uniform solution. The solution is no longer uniform in concentration, some of the salt diffuses toward this portion of the solution, and water moves away from it, until equilibrium is reached and the concentration is again uniform throughout. If the solution contained glucose instead of a salt, and this were being removed and used by a living cell, the result would be similar. Diffusion would tend to restore the uniformity of the solution, which was disturbed by the activity of the cell. If the cell is producing a waste product such as urea, the concentration of this compound in the cell would be higher than in the surrounding medium, and it would tend to diffuse out of the cell. Diffusion, then, is the essential means by which a cell obtains its food and disposes of its wastes.

**Osmotic Pressure.**—The operation of the law of diffusion may be interfered with by the nature of the

membrane which has been described as surrounding the protoplasm. It is well known that artificial membranes may be made which allow water to pass freely, but through which substances in solution pass very slowly or practically not at all. Such a membrane may be made of copper ferrocyanide. If a solution of copper sulfate, for instance, is placed on one side of this membrane, and pure water on the other, there is a tendency for the whole to become uniformly concentrated by a movement of the salt into the water and of the water into the salt solution. Due to the properties of the membrane, only the latter movement is possible. This one-sided movement results in the development of pressure on the solution side of the membrane. This pressure is called osmotic pressure.

**Permeability.**—A membrane allowing the passage of water but entirely preventing that of solutes is said to be semipermeable. No membrane is known that is perfectly semipermeable, and many, such as parchment paper and collodion, only retard the movement of solutes, but do not prevent it entirely. It is characteristic of colloids that they do not diffuse across even such membranes as these. That membranes surround protoplasm has been mentioned. A high concentration of soluble substances within the cell, then, would give rise to a considerable osmotic pressure inside the cell, provided the surrounding medium is a less concentrated solution. This, and the water absorbing capacity of the colloids of the cell are responsible for its "turgor," or the internal pressure which keeps it rigid.



If the membrane surrounding the cell were perfectly semipermeable, no food could reach the cell, and it could dispose of none of its waste products. The membrane is somewhat permeable, and differently permeable to different substances. Not only is this true, but its permeability changes, sometimes very rapidly, under the influence of salts and of acids and alkalies, which, as has been stated, affect the physical nature of the membrane and thus alter its permeability.

**Mass Movement.**—Diffusion is a relatively slow process. It is sufficiently rapid to meet the needs for the transport of materials to and from single cells, and from part to part of very small and relatively simple many-celled organisms, but in larger organisms, should the transport of materials from part to part be dependent on diffusion alone, coördinated life would be impossible, or at least it would be so slow as to be unrecognizable. Conditions favoring the transfer of solutions *en masse* have developed to some extent in plants, and to much greater perfection in the higher animals. A remarkably short time is required for a substance entering the blood stream at one point to reach every cell of the body. Thus the transportation of materials from part to part of the body does not occur by diffusion, but by a mass movement of their solution. The actual taking up or rejecting of these substances by the cells, however, occurs by diffusion, just as it does in the case of the single-celled organisms.

**Other Functions of Water.**—Aside from furnishing the medium by which transportation of materials is possible, water serves other functions in living or-



ganisms. It takes part in chemical reactions such as those of hydrolysis, and is formed by others such as condensation and oxidation. The high specific heat of water is important because it makes changes of temperature relatively slow. Its high heat of vaporization is a great aid in disposing of the excess heat produced by oxidation in animals, and by the absorption of radiant energy by plants.

**Catalysis.**—Many of the reactions which take place in living organisms also may be carried out in the laboratory. Starch may be hydrolyzed to glucose by boiling with acids; at a high temperature, fats may be formed by the condensation of glycerol and fatty acids; in the presence of powerful oxidizing agents and at high temperatures, both fats and carbohydrates may be oxidized to carbon dioxide and water. It should be noted that strong reagents and high temperatures are required for carrying out these reactions in the laboratory. Neither of these conditions is found in living cells, yet here the changes mentioned proceed easily and rapidly. Somewhat similar phenomena are met outside of living organisms. Hydrogen and oxygen, when mixed at room temperature, do not react measurably; only when heated to a rather high temperature do they combine and form water; but if a little very finely divided platinum is introduced into the mixture, combination occurs rapidly at room temperatures. The platinum appears to have taken no part in the reaction, it remains unchanged when the reaction is completed, yet its presence has caused rapid combination to occur, when

under similar conditions practically no change takes place in its absence.

Part of the oxygen of potassium chlorate may be obtained by heating the salt to  $350^{\circ}$ , to drive off the remainder a temperature of over  $600^{\circ}$  is required; but if the potassium chlorate is mixed with manganese dioxide, oxygen is obtained at  $200^{\circ}$ . All the manganese dioxide is still present at the end of the reaction.

A solution of sucrose heated to  $70^{\circ}$  hydrolyzes very slowly indeed, but if HCl is added, hydrolysis at that temperature is very rapid. In this case, too, the substance which hastens the change is not used up, but all of it is present at the end of the reaction.

Substances are known which retard reactions. Thus phosphorus oxidizes slowly in the air; but if a little ether vapor is present, the oxidation is practically stopped.

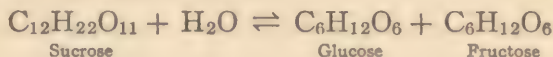
All the reactions mentioned above are examples of the action of catalysts. A catalyst may be defined as a substance which changes the rate of a reaction, but which is not combined with its final products. Catalysts are extremely useful in the chemical industries. As examples may be mentioned the use of oxides of nitrogen or of finely divided platinum in the manufacture of sulfuric acid, and the use of nickel or its compounds in the hydrogenation of unsaturated oils.

**Enzymes.**—Starch is quite a stable substance, and a starch paste, if it is protected from the action of microorganisms, will remain in suspension practically unchanged for a long time. Its hydrolysis to

glucose is brought about by boiling with an acid, which acts as a catalytic agent. If to a starch paste is added a little of an extract of sprouting barley prepared in such a way that no living cells are included, the starch disappears quite rapidly and a reducing sugar is formed, which is found to be maltose. Evidently some substance is present in the malt extract which catalyzes the change from starch to maltose. This substance may be purified partially by precipitating it from the extract with alcohol. It has never been obtained entirely pure, and little or nothing is known as to its exact chemical nature. An interesting fact about this substance is that it is quite specific in its action, aiding the hydrolysis of starch but having no effect on such closely related substances as inulin, hemicellulose, and cellulose.

This active substance in malt extract, which is called amylase, is one of many substances that may be obtained from living organisms, all of which are able to catalyze some chemical reaction. They are called enzymes because some of those first studied were obtained from yeast. Enzymes may be defined as catalysts formed by living cells, but which are able to act independently of the cells. In some cases the enzyme usually acts outside of the cells which formed it, as is true of those which aid in the digestion of food in the alimentary canal. Others usually act within the cell and are separated from it only with considerable difficulty. An example of these is zymase, formed by yeast, which catalyzes the alcoholic fermentation of sugar.

**Reversibility of Enzyme Action.**—Enzymes have been found that hasten most of the hydrolytic reactions that occur in plants and animals. Since hydrolysis and condensation are the opposite directions of the same reaction which tends to reach a point of equilibrium, the same enzyme hastens both reactions. The one which predominates depends on the conditions not on the enzyme. The hydrolysis of sucrose may be taken as an example:



The direction in which the reaction proceeds depends on the relative concentrations of the reacting substances on the two sides of the equation. Thus an increase in the amount of sucrose or water would favor hydrolysis and an increase in the amount of glucose and fructose would favor condensation. In the same way the removal of glucose or fructose would favor hydrolysis and the removal of sucrose or water would favor condensation. The effect of a catalyst on this reaction is to hasten whichever change the conditions favor; so the same catalyst under differing conditions may appear to favor either condensation or hydrolysis.

Although enzymes are catalysts, it is customary to speak of them as causing the changes they catalyze. Thus it is usually said that invertase hydrolyzes sucrose. However it should be remembered that the enzyme is not the active agent in these changes, but only serves to hasten them.



**Properties of Enzymes.**—Enzymes differ quite widely among themselves in properties. Perhaps none of the general properties listed below applies without qualification to all enzymes, but they are sufficiently general to be considered characteristic.

Enzymes are soluble in water and are precipitated by alcohol or acetone. This furnishes a method which is frequently used in purifying enzymes. They are colloidal substances, and therefore do not diffuse through parchment membranes, a property which is also of use in purification.

Living cells are much more sensitive to preservatives than are enzymes. Thus enzyme action may go on in a solution saturated with toluene, in which no bacteria or other organisms will grow. This makes it possible to distinguish between the action of enzymes and that of living protoplasm.

Enzymes are destroyed by heat but they differ considerably in their sensitiveness. Most of them, if they are in solution, are destroyed at temperatures considerably below that of boiling water, but dry preparations are very much more resistant to heat.

Enzymes are most effective as catalysts at a quite definite degree of acidity or alkalinity. This differs widely for different enzymes. Even a slight variation from the most favorable reaction decreases the activity of the enzyme very markedly, and considerable variations are likely to destroy it. It is evident that strong acids or alkalis cannot be used in making enzyme preparations.

The action of enzymes is more or less specific. That



of the ones aiding the hydrolysis of the carbohydrates is especially so. Invertase, which may be obtained from old cultures of yeast, hydrolyzes sucrose, but has no effect on other disaccharides. The enzymes hydrolyzing proteins are less specific, but act on nothing but proteins. It appears that there must be some close structural relationship between an enzyme and the substance on which it acts.

The name given an enzyme is usually formed by adding the ending "ase" to the name of the substance on which it acts; thus amylases act on starch, proteases on proteins, lipases on fats. However, before this system was adopted, many enzymes had been studied and named, and, in most cases, the older names have been retained although they do not follow the modern system of nomenclature.

**Classification.**—The enzymes may be divided into the following classes: hydrolyzing enzymes; coagulating enzymes; decomposing enzymes; oxidizing enzymes. By far the larger number of the enzymes that have been studied belong to the first group. As was stated above, it is probable that all these enzymes bring about condensations or hydrolyses depending on the conditions under which they act. Those hydrolyzing carbohydrates are remarkably specific in their action. There are distinct enzymes hydrolyzing each of the disaccharides. Invertase, or sucrase, is present in the intestinal secretions and maltase is found in the same place; both are widely distributed in plants. Lactase also is present in the intestine but it is very rare in plants. An amylase occurs in the saliva, and another

in the pancreatic juice. Amylases also occur very generally in plants. Apparently enzymes hydrolyzing hemicelluloses do not occur in animals, but some of this material disappears during digestion, due to bacterial action. In plants, however, hemicelluloses are hydrolyzed readily. Neither higher plants nor animals appear to form enzymes capable of hydrolyzing cellulose, but some of the lower forms of plant life are able to decompose this very resistant carbohydrate.

An enzyme aiding the hydrolysis of fats is present in the pancreatic juice. Lipases also are widely distributed in plants, especially in certain seeds that are rich in fats. These enzymes hydrolyze nearly all fats, as well as some esters that are not fats, such as ethyl acetate.

Several different enzymes hydrolyzing proteins are known. One occurs in the gastric juice, another in the pancreatic juice, and a third in the secretions of the intestinal glands. Proteases also occur in certain fruit juices, such as that of the pineapple, and in many seeds. Certain of these enzymes act most readily on the native proteins; others attack proteoses and peptones more readily.

Examples of coagulating enzymes are rennin, which occurs in the stomach particularly of young mammals, and which aids in the coagulation of the casein of milk, and thrombin, which is an important agent in the clotting of blood.

Decomposing enzymes aid in somewhat more deep-seated changes than those that have been described. As an example, zymase of yeast may be mentioned.

This enzyme aids in the decomposition of glucose and some other sugars into ethyl alcohol and carbon dioxide. It can be separated from yeast cells, but when used practically this separation is not attempted, and the yeast cells themselves are grown in the solution containing the sugar. At present this is the principal commercial method for the manufacture of alcohol.

Only a few specific oxidizing enzymes are known: one of these is Xantho-oxidase, which brings about the oxidation of xanthine to uric acid. Two other classes of oxidizing enzymes are described. The peroxidases are able to liberate oxygen from hydrogen peroxide or from organic peroxides, and use it to oxidize certain aromatic compounds closely related to phenol. The products of this oxidation are often colored. It is due to such a change that the cut surfaces of apples and potatoes darken on exposure to air. Peroxides are formed by the action of the oxygen of the air on some of the organic compounds present; they are then decomposed by the peroxidases, liberating atomic oxygen, and this oxygen acts on certain aromatic compounds, forming colored products.

Catalases are able to liberate molecular oxygen from hydrogen peroxide. The foaming of hydrogen peroxide when placed on a wound is due to the liberation of oxygen by the catalase of the blood.

Although both of these types of oxidizing enzymes are very widely distributed in living organisms, it is uncertain whether they have anything to do with the oxidations which are so important in furnishing the energy used by living cells. So far as is known, the

peroxidases aid in the oxidation only of the aromatic substances that have been mentioned, and have no effect on the sugars or fats, which are the principal sources of energy. The catalases seem to be able to liberate only molecular oxygen, which is relatively inactive.

No enzymes have been found which aid many of the reactions going on in living organisms, but it seems very probable that such enzymes do exist for most, if not for all, of these reactions.

## CHAPTER XIII

### THE CHEMISTRY OF PLANTS

The plant kingdom includes an extremely wide variety of forms, differing greatly in size and complexity. These range from microscopic single-celled plants such as yeasts, to the giant sequoia trees of California. This chapter will deal principally with the chemistry of the green flowering plants, as these include most of the more familiar species and practically all of the cultivated plants. These plants are usually propagated by seeds.

**Composition of Seeds.**—In general, seeds are composed of three essential parts: the embryo, which under proper conditions is able to develop into a new plant; a store of materials which can support the growth of the embryo; and a protective covering. The nature of each of these parts differs considerably in seeds of different species, but the essential features are much the same in all, and the process of germination involves the same types of changes in all cases.

Usually much the larger part of the seed is filled with reserve food materials, including carbohydrates, fats, proteins, and certain mineral elements.

Of the carbohydrates, only a relatively small amount



is soluble. This varies widely in different seeds: in the pumpkin it amounts to about 3 per cent; in soy beans 7 or 8 per cent; in lupines 14 to 16 per cent; in sweet corn, sucrose alone may amount to 11 per cent of the weight of the seed. Reducing sugars are usually absent or present only in traces. Sucrose and raffinose are very widely distributed; and other trisaccharides and possibly also tetrasaccharides occur. Insoluble carbohydrates are much more abundant. In the starchy seeds, such as grains, starch may comprise 50 to 80 per cent of the weight of the seed, and occurs in lesser amounts in many other seeds. The walls of the cells in which starch is stored, beside containing cellulose, are more or less thickened by deposits of hemicellulose, which is hydrolyzed quite easily by the action of dilute acids or of enzymes. In some of the legumes, and in the date, ivory nut, and other seeds, hemicellulose is the principal form of carbohydrate reserve. The usual products of the hydrolysis of these hemicelluloses are mannose, galactose, and frequently a pentose, which is usually arabinose.

In some seeds fats are more abundant than the carbohydrates; in fact various seeds are the principal sources from which the oils used commercially are obtained. The seeds of cotton, flax, corn, and soy beans are important sources of fats. The fat stored in a seed is quite characteristic of the species; some of the differences that obtain have been mentioned.

Of the nitrogen compounds of seeds, only a small part is nonprotein, including a small amount of amino acids, some proteose and peptone, and usually a small

amount of such other compounds as alkaloids. The protein content of seeds varies as widely as that of the other constituents. Often seeds that are rich in fats also are high in protein. Thus the cake remaining after pressing out the oil from various seeds furnishes some of the richest protein feeding stuffs; flax-seed meal and cotton-seed meal are examples. Leguminous seeds also are rich in proteins.

Mineral elements are not as abundant in seeds as they are in growing plants, and the relative amounts of the different elements are not the same. Phosphorus and potassium are usually present in largest amounts. Possibly a considerable amount of the former is in combination with inosite as phytin. The relation between calcium and magnesium is especially interesting; magnesium is often considerably in excess of calcium in seeds, but in leaves and other parts of growing plants, the reverse is usually the case.

**Conditions for Germination.**—A seed, then, is a small living plant in a dormant condition, provided with reserve food materials which are able to support the young plant for some time after active growth begins. Provided that the embryo is mature and in a healthy condition, its growth will begin whenever certain necessary conditions are met. The most important of these is moisture, as rapid growth is impossible except in the presence of large amounts of water. Certain seeds germinate poorly because their seed coats are very impervious and water is unable to reach the embryo. This condition is quite common among the legumes. To avoid poor germination from this cause,

the coats of such seeds as sweet clover are weakened by scarifying, which is done by blowing them against a rough surface.

The best temperature for germination varies quite widely for different seeds. In many cases, rather rapid alternations of temperature are found to hasten germination.

Oxygen is essential to germination as it is to growth of any kind, but the amount of free oxygen required varies greatly. Some seeds germinate under water where the supply of oxygen must be very limited; in other cases, such as the cocklebur, germination may be delayed because the seed coat is only slightly permeable to oxygen. In such cases, an increase in the partial pressure of oxygen in the air hastens germination.

There are some seeds whose germination is favored by light, but it seems doubtful if light is absolutely essential to the germination of any seeds.

**Germination.**—The first increase in size of seedlings is due to the absorption of water. Within a day or two the moisture content of the embryo may increase from 5 per cent to 90 per cent. This results in a great increase in size before cell division begins, and provides conditions favorable for cell division and for the action of enzymes. The appropriate enzymes develop rapidly and attack the insoluble reserve food substances stored in the seed. This is a process of digestion, the preparation of food materials for absorption and use by the growing cells of the embryo. As has been stated, digestion is principally an hy-

dolytic process by which complex, often insoluble, materials are changed to their simpler soluble components.

**Digestion of Carbohydrates.**—The principal enzymes acting on the carbohydrates are invertase, amylase, maltase, and cytase, which bring about the hydrolysis respectively of sucrose, starch, maltose, and hemicellulose. The final products of their activity are monosaccharides, glucose, fructose, galactose, and mannose. Whatever simple sugars are formed, so far only glucose has been shown to be present in the seedling. It is possible that the other sugars are changed to glucose before being used, or that they are used more rapidly than glucose, and so only the latter is present in amounts sufficient to be detected. Sucrose decreases during the first few days of germination, but later increases. It appears that the sucrose must be formed from the products of hydrolysis of starch or hemicellulose.

**Digestion of Fats.**—The fats in seeds are hydrolyzed by the enzyme lipase. During germination the amount of free fatty acid, both in the seedling and in the places where reserve foods are stored, increases rapidly. The glycerol that is formed by the hydrolysis of the fats disappears. Both the glycerol and the fatty acids are changed, in part at least, to sugars before being used. It seems that in the presence of a little soap or similar substance, fatty acids and neutral fats are able to diffuse through the cell walls from the storage region to the seedling. Thus not all the change from fat to sugar occurs in the storage



region. By comparing the formula for a fatty acid with that for a sugar, it will be seen that an important feature of the change is the addition of oxygen. This change liberates considerable amounts of energy which may be used by the seedling.

**Digestion of Proteins.**—The reserve proteins of the seed are hydrolyzed by the appropriate enzymes to the amino acids of which they are composed. It is possible that a certain amount of these products is used directly by the cells of the seedling in constructing the proteins required for its growth. But a considerable part of them appears to be changed to temporary intermediate products. These are asparagine,



the acid amides respectively of aspartic and glutamic acids, which are usually present among the products of hydrolysis of proteins. Asparagine is usually present in seedlings in much greater amount than is glutamine. These compounds furnish the growing cells with combined nitrogen which, in the presence of simple sugars, may be built up into proteins.

**The Use of Minerals.**—The supply of mineral elements in the seed is relatively less abundant than that of the organic food substances. A considerable part of these minerals is transported to the seedling and used by it in the early stages of its growth. A large part, too, remains in the storage organ, where it seems to be necessary to the activity of the enzymes



digesting the food reserves. The root of the seedling very early comes in contact with the soil solution, from which it takes up not only a supply of water but also of mineral elements. Thus the seedling very soon becomes independent of the supply of minerals in the seed.

**Photosynthesis.**—Soon after the young shoot is exposed to the light, it turns green due to the development of a pigment called chlorophyll. In its chemical structure this pigment resembles the red coloring matter of the blood somewhat, containing groupings like that found in the amino acid proline. Chlorophyll differs from the blood pigment in containing magnesium, whereas the latter contains iron. It is through the agency of this pigment that green plants acquire a function peculiar to themselves, and which is of the greatest possible importance to animals as well as to plants. This is called photosynthesis, or carbon assimilation.

It is evident that the supply of organic food materials in the seed is limited, and therefore the plant cannot continue to grow indefinitely at the expense of these reserves. If it is to go on growing, new sources of supply of food substances must be found. It is in this particular, their source of organic food, that green plants differ from other organisms. Other plants and animals use as food organic compounds in whose synthesis they take no part. Green plants are like other plants and animals in all essential respects, but they have the added function of synthesizing their own organic food.

**The Raw Materials.**—Water and carbon dioxide are the raw materials used in this synthesis. The water is obtained from the soil, it is taken up by the roots and carried through the conducting system of the root and stem to the leaves. A large part of the water reaching the leaves is evaporated from their surface, but part of it is retained and used by the cells containing chlorophyll in the synthesis of organic compounds.

The carbon dioxide is obtained from the small amount of this compound present in the air. It diffuses into the leaf through the small openings, or stomata, in the leaf surface, from which it reaches the chlorophyll-containing cells, where it is dissolved in the abundant supply of water that the cells contain.

**The First Product.**—The first recognizable product of the synthesis is a sugar. Just which sugar is formed first is somewhat uncertain, but it is probably either glucose or sucrose. For convenience in the further discussion of the subject, it may be considered that glucose is the first sugar formed in photosynthesis. From this first product, the plant is able to build up all the great variety of organic compounds of which it is composed.

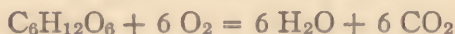
In very many plants, starch appears in the chlorophyll-containing cells almost as soon as photosynthesis begins. By dissolving out the coloring matter with alcohol and then treating the leaf with iodine, the presence of starch is easily recognized by the intense blue color produced. This test for starch is often used in demonstrating photosynthesis. In many plants, however, no starch is formed, and in any case it must

be considered as a secondary product, formed by the condensation of the sugar which is the first product of the synthesis. Starch seems to be a form in which the products of photosynthesis are stored temporarily when they are formed faster than the plant uses them. Since photosynthesis occurs only in the light, this reserve may be used to support the continued activities of the plant during the hours of darkness.

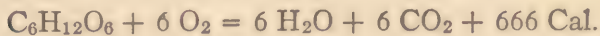
**The Energy Relations.**—Considering glucose as the first product of photosynthesis, its formation may be indicated by the following equation:



As a matter of fact, oxygen is given off from a leaf during photosynthesis, and approximately in the amount indicated in the above equation. It will be noticed that this equation is the reverse of that representing the complete oxidation of glucose:

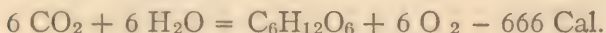


The oxidation of glucose, like that of other organic compounds, liberates large amounts of energy. The oxidation of one gram molecule of glucose (180 g. liberates 666 Calories of heat. To represent the changes of energy as well as those of matter, the equation is written:



Now if the oxidation of glucose to carbon dioxide and water liberates this large amount of energy, its formation from carbon dioxide and water must require

the same amount, and the equation for the synthesis of glucose would be:



In order that the synthesis may occur, this energy must be supplied. Its source is indicated by the name that has been given the process, photosynthesis. In the presence of the green coloring matter, chlorophyll, the light energy of the sun is converted into chemical energy. This energy is used to bring about the reduction of carbon from its completely oxidized condition in carbon dioxide to its partially reduced condition in glucose. The kinetic energy of light has been changed to the potential energy represented by glucose and oxygen. On the recombination of these two products of the reduction, resulting in the oxidation of glucose, this potential energy is liberated, and may be used by living organisms in carrying on their characteristic functions.

**Importance of Photosynthesis.**—Thus, by this process of photosynthesis, green plants are able to manufacture their own organic food with the aid of the energy furnished by the sun. But the importance of the process is much greater than this would indicate. All other plants, and all animals, either directly or indirectly, use green plants as their only source of food. Thus green plants supply the organic building material and energy for all living organisms. Not only does photosynthesis furnish the energy which makes life possible, but also wood, coal, petroleum, and gas are products of green plants. With the excep-



tion of water power and wind, all energy used in heating and lighting, in running automobiles, railroads, and factories, was derived from the sun and stored in the form of reduced carbon compounds by the process of photosynthesis carried on by green plants in bygone ages.

**The Carbon Dioxide Supply.**—Considering the enormous number of green plants that are growing continually, immense amounts of carbon dioxide must be taken from the air daily. The amount of this gas present in the air is relatively small, three or four parts in 10,000. It would seem that this supply might become exhausted, that all the carbon would be fixed in organic compounds, and that photosynthesis then must cease. Undoubtedly this would happen in a relatively short time were it not that carbon dioxide is being returned to the air constantly. The most important factors in this return may be listed as follows: Combustion, carbon dioxide is one of the products formed when fuel is burned. Decay, the final products of decay are the same as those of combustion. Respiration, the oxidation of organic compounds in living cells contributes immense amounts of carbon dioxide to the air. Volcanoes and springs also give off large amounts of carbon dioxide. So accurately is the replenishing of the carbon dioxide of the air balanced against its use by green plants, that no perceptible change in the amount of this gas in the air has occurred since accurate determinations of it have been made.

It has been shown that, in many cases, a higher

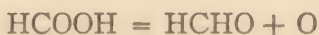


concentration of carbon dioxide in the air, up to 5 per cent or more, increases the rate of photosynthesis and of plant growth. Attempts have been made to make use of this fact commercially. The flue gases from factories are rich in carbon dioxide, and these gases have been conducted to the surface of the soil of near-by gardens, thus increasing the concentration of carbon dioxide in the air surrounding the growing plants. Certain other constituents of the flue gas that are toxic to plants, such as sulfur dioxide, must be removed first. Experiments of this kind have not gone far enough as yet to prove that the method is practicable.

**Possible Intermediate Compounds.**—It is probable that the change from carbon dioxide to glucose is not a direct one, but that intermediate compounds are formed. Many theories have been advanced as to the nature of these, but none of them is sufficiently supported by experimental facts to be considered established. As simple and direct as any of the theories is that according to which formaldehyde is one of the intermediate compounds. Carbonic acid is formed when carbon dioxide is dissolved in the water present in the chlorophyll-containing cells. The first step in the reduction is the changing of this compound to formic acid:

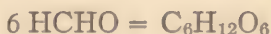


The formic acid then is reduced to formaldehyde:



The chemical energy required for these reductions is obtained by the transformation of the light energy of the sun through the agency of chlorophyll. Both of these products are toxic to plants, but they do not accumulate in amounts sufficient to be injurious, because they are changed at once to other nontoxic compounds.

Formaldehyde has the same percentage composition as glucose, and its carbon atom is in the same state of oxidation as the carbon atoms in glucose. The tendency of aldehydes to polymerize has been mentioned. In the laboratory it is possible to cause formaldehyde to polymerize to compounds having the same formula as glucose. If this occurs in the plant, the change would be represented by the following equation:



According to this theory, then, formaldehyde is the first product of photosynthesis, since it is the first compound formed in which the carbon is in the same state of oxidation as it is in glucose.

**Uses of the Products of Photosynthesis.**—The products formed by photosynthesis are used by the plant principally in three ways: in respiration, in growth, and in the storage of reserve materials which may be used for future growth.

**Respiration.**—Since respiration is the oxidation of organic substances with the liberation of energy, it is exactly the opposite of photosynthesis. In respiration, oxygen is used and carbon dioxide and energy

are liberated; in photosynthesis, carbon dioxide and energy are used and oxygen is liberated. Respiration goes on at all times in all living cells; therefore it occurs at the same time with photosynthesis in the leaves of green plants. In general the rate of respiration of an organism parallels its activity. Thus germinating seeds and opening flowers respire very rapidly; resting seeds and parts of plants that have reached their full growth respire very slowly. The proportionality between rate of respiration and activity is by no means absolute, and it is probable that, in many cases, much of the energy liberated by respiration is not used directly by the plant, but is lost by radiation as heat, or in the evaporation of water.

**Growth.**—In being used for growth, the first products of photosynthesis undergo very decided changes in forming all the different compounds of which a plant is composed. In growth, new protoplasm is formed, and new nonliving supporting structures are laid down. The latter increase much more rapidly than the former, especially as the plant nears maturity.

**Carbohydrates.**—Aside from the sugars dissolved in the plant juices, the most abundant carbohydrates are hemicellulose and cellulose. Cellulose is a condensation product of glucose, but the hemicelluloses are formed by the combination of a number of different sugars. Galactose, mannose, and arabinose are especially abundant. These sugars must be formed from glucose before the hemicelluloses can be built up. The formation of these carbohydrates involves

rearrangement and condensation, but not reduction or oxidation, except possibly in the formation of arabinose.

Compound carbohydrates such as lignocellulose, pectins, and gums also are present in large amounts. Both oxidation and reduction are concerned in the formation of the noncarbohydrate part of these substances. The acids which form a part of the pectins and gums are oxidation products of the carbohydrates, and the methyl groups present in lignocellulose and the pectins are more completely reduced than the sugars. Thus the principal changes accompanying the formation of the structural carbohydrates of plants from the products of photosynthesis are rearrangement and condensation. Some oxidation and reduction occur, but they are of minor importance.

**Fats.**—The differences between fats and sugars have been discussed. The carbon atoms in fats are much more completely reduced than those in the sugars, as is indicated not only by the formulas for the two groups of compounds, but also by the great difference in the amount of energy liberated by their oxidation. The oxidation of a gram of fat liberates more than twice as many calories as that of a gram of glucose. It is evident that the formation of fats from glucose is a reduction process which requires large amounts of energy. The oxidation of part of the glucose present probably furnishes the energy needed for the conversion of another part to fats.

**Proteins.**—The changes concerned in the build-



ing up of proteins in plants are much more complex than those that have been described for carbohydrates and fats. The average state of oxidation of the carbon atoms of proteins is intermediate between that of the fats and of the carbohydrates. Some reduction, therefore, occurs in the formation of proteins, or of the amino acids of which they are composed, from the first products of photosynthesis. Beside carbon, hydrogen, and oxygen present in the carbohydrates, proteins contain two other elements, nitrogen and sulfur, and many of them also contain phosphorus. These elements are obtained from their inorganic compounds in the soil. Together with other salts, they enter the roots by diffusion and are transported to various parts of the plant where they are used.

Nitrogen is taken up from the soil by plants largely in the form of nitrates. The nitrogen in these compounds is in its most highly oxidized condition, having a positive valence of five. Beside being combined with organic compounds, it must be reduced to its lowest state of oxidation in which it exists in the proteins, and in ammonia and its compounds, where it has a negative valence of three. This reduction is also an energy consuming reaction. Some plants are able to use ammonium salts directly as sources of nitrogen, but whether this occurs naturally to any great extent is uncertain. Leguminous plants, such as beans, peas, and clover, sometimes have colonies of bacteria growing on their roots, through whose agency these plants are able to use the free nitrogen of the air. Since combined nitrogen is scarce and expensive, this fact



is of great importance in maintaining the fertility of the soil.

Plants take up sulfur from the soil in the form of sulfates. In these compounds sulfur has a positive valence of six, which is its highest state of oxidation. The sulfur occurring in such constituents of the proteins as cysteine has a negative valence of two; hence the introduction of sulfur into proteins also involves reduction.

Phosphorus is obtained from the soil in the form of phosphates, and it is present in the proteins in the same state of oxidation.

From this brief discussion, it is evident that the principal changes accompanying the utilization of the products of photosynthesis by plants for growth are condensations and reductions. Their utilization for respiration involves oxidation.

The composition of plants changes during growth, especially as maturity is reached. The content of water, of living protoplasm, and of soluble materials decreases, and that of the carbohydrates and compound carbohydrates most resistant to hydrolysis, such as cellulose and lignocellulose, increases.

**Storage.**—Under favorable conditions, plants synthesize more organic food than they use in respiration and growth. This excess accumulates in various parts of the plant, and may be used to support new growth during a later season, until new plants or shoots have developed sufficiently to manufacture their own organic food. The most important place of storage is in seeds, whose composition and germination have

been discussed. Biennials lay up stores of food in roots and tubers; and perennials, such as shrubs and trees, often store large quantities in stems and roots.

The general nature of the changes which the products of photosynthesis undergo during the formation of these storage substances are the same as have been described as occurring during growth. Carbohydrates, fats, and proteins all are formed in varying amounts in different plants. The carbohydrates formed are in general much more easily hydrolyzed than those laid down in the supporting framework. Starch, inulin, and the more easily hydrolyzed hemicelluloses are abundant. Sucrose is the most important of the sugars that occur as reserve food.

**Other Plants.**—The green flowering plants, whose chemistry has been discussed briefly in this chapter, include all the most important crop plants, but they make up only a part of the whole plant kingdom.

There are a great many green plants that do not belong to this group, among which are the algae, mosses, and ferns. Like the flowering plants, these synthesize their own organic food and contribute to the world's supply of reduced carbon. In fact it was the nonflowering green plants whose remains accumulated and formed the immense coal measures.

Aside from these, there are immense numbers of species of plants that contain no chlorophyll and are not able to synthesize their own organic food, but, like animals, live on the organic compounds that have been built up by green plants. If they obtain their food from living plants or animals, they are called parasites;

if from nonliving organic substances, they are called saprophytes.

**Bacteria and Fungi.**—The most important of the plants of this kind are those that are very small and relatively simple in structure, belonging to the two great groups, bacteria and fungi. The bacteria are single-celled organisms, the fungi include both single-celled species and those of more complex structure. Most of them are small, but some forms, such as toadstools and mushrooms, attain a considerable size.

These plants themselves or the spores that many of them form are present practically everywhere. Whenever conditions such as food supply, moisture, and temperature are favorable for them, they grow rapidly, bringing about very decided changes in the medium in which they grow. They digest the organic foods that are available, and use part of the products of digestion for respiration and part for growth. Since they are not able to rebuild organic food with the storage of energy from the sun, the net result of their activity is destructive.

They are the most important agencies in the decay of plant and animal remains. Decay is a process of oxidation caused by the respiration of these organisms, resulting in the formation of carbon dioxide and water from the organic substances they use as food. The continued accumulation of plant and animal remains would soon result in the exhaustion of the carbon dioxide of the air, and the growth of green plants would cease. But, due in large part to the activity of bacteria and fungi, these organic remains are oxidized,

contain is returned to the air as carbon dioxide, making possible again the growth of green plants, the formation of a new supply of organic compounds, and renewed storage of energy from the sun.

their potential energy is liberated, and the carbon they

## CHAPTER XIV

### THE CHEMISTRY OF ANIMALS

**The Source of Food.**—The entire dependence of animals on the synthetic power of green plants has been mentioned. The organic compounds formed by green plants, together with oxygen, contain potential energy which is liberated when these combine in the process of respiration. This is the only source of these compounds and of the necessary energy stored in them which is available to animals. Plant products themselves form a large part of the human diet, and the rather large amounts of animal products also included owe their origin to the plants which the animals producing them used as food. The nature of the compounds has been changed somewhat, but their atoms have been put together first by the aid of plants, and they derive their energy value from the sun through the agency of chlorophyll.

Of the materials used as food, very few are in a condition to be absorbed and used directly by the human body. Just as the reserves stored in seeds must be changed to their simpler soluble components before they are used by the seedling, so the materials comprising human food must be changed, principally by



hydrolysis, to their simpler components before they can be absorbed into the blood stream and used by the cells of the body. This preparation of food for use by the body is digestion. All the three groups of compounds, carbohydrates, fats, and proteins, are used as food, and the digestion of each is carried on by the appropriate enzymes in the alimentary canal.

**Digestion of Carbohydrates.**—The principal carbohydrate used as food is starch. This occurs in plants in the form of dense granules which are not at all easily attacked in the human digestive tract, partly at least because they offer comparatively little surface to the action of the digestive enzymes. When starchy foods are cooked, these granules burst, leaving the starch of which they are composed in a much more finely divided condition, and so exposing an immensely larger surface to digestive action. During cooking, especially baking, there is also some change of starch to dextrin. It is evident that cooking starchy foods makes them much more easily digestible.

**Salivary Digestion.**—In the mouth, beside being divided finely by chewing, the food is mixed with saliva, which is a somewhat viscous liquid secreted by the salivary glands. Its flow is stimulated by the presence of food in the mouth, and also may be stimulated mechanically by inert substances such as sand or paraffin, chemically by acids, or psychically by the sight or smell of food. The amount secreted daily varies greatly but is usually between 1,000 and 1,500 cc. The amount of solids present is very small, about 0.5 per cent, including some salts, largely phosphates,

which give the saliva a neutral or slightly alkaline reaction. Small amounts of albumin and globulin are present, but the organic matter is largely mucin, a glycoprotein, to which the stringy character of the secretion is due. Aside from these constituents, saliva contains an enzyme, ptyalin.

Mastication aids in getting the food into a fine state of division, so that it presents a large surface to the action of digestive enzymes, and also, by mixing the food mass with saliva, begins its dilution with water. This dilution continues in the stomach and small intestine.

Ptyalin is an amylase, that is it brings about the hydrolysis of starch to maltose. It acts best in a neutral or very slightly acid medium, but is destroyed in 0.0001 N or stronger hydrochloric acid. Food does not remain in the mouth long enough for this enzyme to hydrolyze a great deal of the starch, but the action is begun; this is evidenced by the sweet taste developed by starchy food if it is chewed for a considerable time.

**Changes in the Stomach.**—After entering the stomach, the food gradually becomes mixed with the gastric juice which is secreted by small glands scattered about the walls of the stomach. Like saliva, it is very largely water, containing only 2 per cent to 3 per cent of solids. Part of this is inorganic, including chlorides and phosphates of calcium, potassium, magnesium, and sodium and, which is especially remarkable, about 0.3 per cent of free hydrochloric acid.

The organic constituents include enzymes acting on fats and proteins, which will be discussed later.

The mixing of the food mass with the gastric juice is rather slow, and it is some time before the whole mass becomes so acid as to stop the action of ptyalin. Due to this enzyme, there is a very considerable digestion of starch in the stomach. There is no enzyme in the gastric juice which acts on carbohydrates. When the contents of the stomach have become distinctly acid, some sucrose may be hydrolyzed due to the catalytic action of the acid. Other disaccharides are much more resistant to hydrolysis by acids, and are not affected appreciably.

During its stay in the stomach, large quantities of water are added to the food mass, and it enters the intestine as a thin fluid in which the partially digested food materials are dissolved or suspended.

**Digestion in the Small Intestine.**—The secretion from the pancreas, that from the glands along the walls of the intestine, and the bile, are emptied into the small intestine and mixed with the food. These secretions are all more or less alkaline in reaction; so the acid from the stomach is neutralized gradually, and the reaction of the food mass changes slowly from acid to neutral, and then to slightly alkaline.

The small intestine is the principal digestive organ. An amylase in the pancreatic juice, amylopsin, attacks the starch that has escaped the action of ptyalin, changing it to maltose. The secretions of the intestinal glands contain invertase, maltase, and lactase, which bring about the hydrolysis respectively of sucrose,

maltose, and lactose, converting them into their constituent monosaccharides. Thus all the digestible carbohydrates of the food are changed to monosaccharides, and are absorbed as such into the blood stream mainly through the walls of the small intestine.

**The Digestion of Fats.**—A lipase is present in the gastric juice; this enzyme is able to act only on fats that are emulsified, such as those of egg yolk and milk, which are hydrolyzed to glycerol and the fatty acids of which they are composed. The digestion of fats is by no means complete in the stomach, and their hydrolysis is completed in the small intestine by the action of the enzyme steapsin which is secreted by the pancreas. This enzyme is aided by the salts of certain organic acids which occur in the bile. These salts seem to help the digestion of fats in two ways: they have a distinct activating effect on the enzyme, and they aid in the emulsification of the fats. Emulsification increases enormously the surface of the fat exposed to the action of the steapsin.

Of the products of the hydrolysis of fats, glycerol is soluble in water. The fatty acids are insoluble, but their soaps, more or less of which are formed in the alkaline medium of the intestine, are soluble, and are able to aid in the emulsification of fats and fatty acids. The products of hydrolysis, probably held in solution by the bile, are absorbed through the walls of the small intestine into the lymphatic circulation. On passing through the intestinal walls, the glycerol and acids are recombined, and they appear in the lymph as neutral fats.



**Digestion of the Proteins: Gastric Digestion.—**

The proteins are acted on very little, if at all, by the saliva. The enzyme pepsin, occurring in the gastric juice, is able to hydrolyze proteins rapidly in the presence of hydrochloric acid. Some amino acids may be formed by the action of pepsin on proteins, but the principal products are proteoses and peptones; in fact there seem to be some combinations of amino acids that this enzyme is unable to separate. The time the food remains in the stomach is not long enough for the digestion of proteins even to proteoses and peptones to be at all complete.

Especially in young animals, the gastric juice has the power to coagulate milk. It is the casein of milk that is affected, and the action consists of the splitting of one molecule of casein into two of paracasein. It is, then, an hydrolysis. The paracasein forms an insoluble salt with calcium, which separates in the form of a gelatinous curd. The enzyme causing the formation of paracasein is called rennin, though it is uncertain whether it is entirely distinct from pepsin. Rennin is prepared commercially from the lining of the fourth, or true, stomach of the calf, and is used in cheese making.

**Changes in the Small Intestine.—**Digestion of the proteins is continued in the small intestine by two enzymes, trypsin and erepsin. The forerunner of trypsin, called trypsinogen, is secreted by the pancreas. The secretion of the pancreas is mixed with that of the intestinal glands, which contains a substance called enterokinase which is not an enzyme, but acts on



trypsinogen, changing it into the active trypsin. Acting in a neutral or slightly alkaline medium, trypsin attacks proteins in much the same way as pepsin, but its action is much more complete. All the digestible protein is changed to proteose and peptone, and a considerable amount of amino acids is formed. The final steps in the digestion are brought about by erepsin which is secreted by the intestinal glands. It acts rapidly on proteoses and peptones, hydrolyzing them to their constituent amino acids. Amino acids are the final products of the digestion of proteins, and they are absorbed through the walls of the small intestine into the blood stream.

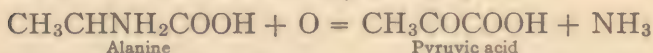
**Antiseptic Action of the Gastric Juice.**—The cooking of foods improves their flavor and, especially in the case of starch, it makes them more easily digestible. It also destroys large numbers of bacteria always present in foods. Since many foods are eaten raw, and since bacterial contamination of cooked foods before eating cannot be avoided entirely, the food as it reaches the stomach always contains many of these microorganisms. Most of them are unable to live in the strongly acid medium of the normal gastric juice. The strong antiseptic power of the gastric juice is important in more ways than one. It lessens very greatly the danger of contrasting food-borne diseases such as typhoid fever, and prevents the formation by bacteria from the food, of products such as organic acids and gases, which sometimes cause a great deal of discomfort when the gastric juice is not sufficiently acid to stop the action of these organisms.

**Bacteria in the Intestine.**—Normally when the food mass leaves the stomach it is nearly free from living bacteria. As has been stated, the secretions entering the intestine are alkaline, and the contents of the intestine gradually decrease in acidity and then become slightly alkaline. This, the body temperature, and the large amount of water present supply conditions that are very favorable for the growth of bacteria, and their numbers increase rapidly as the food passes along the intestine.

The bacteria developing in largest numbers at first are those attacking carbohydrates and forming organic acids, such as butyric and lactic, and usually some methane and hydrogen. As these organisms attack the soluble carbohydrates most readily, their action causes a loss in the nutritive value of the food. They also act on some of the indigestible carbohydrates. The products formed by these bacteria gradually change the reaction of the intestinal contents, which was slightly alkaline in the upper small intestine, to slightly acid before the large intestine is reached. In the digestive tract of herbivorous animals, a large part of whose food consists of carbohydrates, this is the prevailing type of bacterial action throughout.

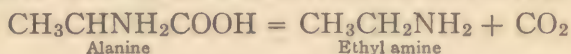
The food of carnivorous animals contains little carbohydrate and much protein, so that the organisms forming acids from carbohydrates have little chance to develop. Instead, the putrefactive bacteria which attack proteins multiply very rapidly. Acting on the amino acids, several types of changes may be caused. The removal of the amine group gives rise to the

corresponding ketone acid, which may be absorbed into the blood stream and used by the body:



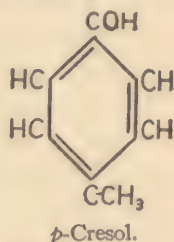
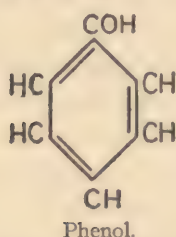
Some at least of these ketone acids may be reduced by bacterial action to the corresponding fatty acids.

A second type of action on the amino acids is the removal of carbon dioxide from the carboxyl group:

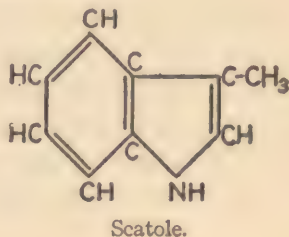
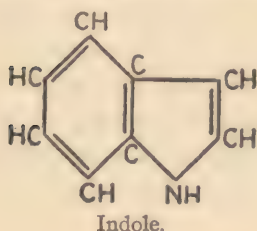


This results in the formation of amines. These amines, formed from proteins by bacterial action, are called ptomaines.

In some cases both of the changes just mentioned occur and then may be followed by the removal of methyl groups. By such combinations of reactions, tyrosine may give rise to *p*-cresol and phenol:



and tryptophane to skatole and indole:



Although some bacterial action occurs in the small intestine, it becomes much more prominent in the large intestine where the undigested residues of the food are acted on. Large amounts of water are reabsorbed through the walls of the large intestine, and also many of the products of the action of bacteria on the food residues. Some of these, such as the organic acids, may be used in the body as sources of energy, but many of the products of the putrefaction of proteins are decidedly toxic, and, if they accumulate in considerable amounts, their effects may be very serious. This is especially true in constipation, when the food residues are subjected to bacterial action for a long time.

The feces are not simply the undigested portion of the food, but they contain, up to perhaps one-third of their dry weight, the bodies of bacteria which have grown at the expense of the undigested portion of the food. They also contain some of the products of bacterial action, and much of the solids contained in the digestive fluids that have been mixed with the food in the course of its passage through the alimentary canal.

In omnivorous animals, such as man, the type of bacterial flora predominating in the intestine depends largely on the diet, and may be changed more or less at will by changing the nature of the food used. Since this controls the amount of putrefaction occurring in the food residues, it is one of the very important effects of diet on health.

**Absorption.**—Some of the products of the digestion of food are probably absorbed into the blood stream through the walls of the stomach; but as digestion is far from complete in this organ, the amount of material absorbed is quite small. Probably 85 or 90 per cent of the digested food is absorbed through the walls of the small intestine.

In the large intestine, water is reabsorbed rapidly, and many of the products of bacterial action pass the intestinal walls into the blood.

The sugars are absorbed as monosaccharides, glucose, fructose, and galactose, into the capillaries leading to the portal vein, and follow this path to the liver.

The fats, as glycerol and fatty acids, held in solution by the bile salts, enter the cells of the walls of the small intestine, where they are resynthesized into neutral fats, and passed on into the lymph. After a meal rich in fats, this has a milky appearance and is called chyle. It follows the lymphatic circulation by way of the thoracic duct and enters the blood stream at the juncture of the thoracic duct with the jugular vein.

During digestion the proteins have been hydrolyzed completely to amino acids, which are absorbed into the capillaries leading to the portal vein, and thus reach the liver, through which they pass, and are distributed to all parts of the body by the blood stream.

**Composition of the Blood.**—As far as nutrition is concerned, the most important function of the blood is that of transportation. It is composed of a liquid, the plasma, which contains certain proteins, albumin,



globulin, and fibrinogen, and salts, of which phosphates, chlorides, and carbonates are the most important. In the plasma are suspended two kinds of cells: the nucleated, amoeboid white cells have among their functions that of protection against invading bacteria; and the non-nucleated red cells contain hemoglobin, a conjugated protein containing iron, which is concerned in the transportation of oxygen. Of the inorganic substances, potassium salts are especially abundant in the corpuscles, and those of sodium in the plasma. The phosphates and carbonates serve to maintain the slightly alkaline reaction of the blood. In spite of the fact that carbon dioxide and other acid substances are being formed in the body constantly, the reaction of the blood does not change appreciably, due in part to the very efficient regulatory action of these salts, and in part to the constant elimination of these acid substances through the lungs and kidneys.

**Functions of the Blood.**—Aside from the constituents mentioned, the blood carries the food substances, sugars, fats, and amino acids, and oxygen to the manufacturing centers of the body. Beside certain special organs, such as the liver, in which a large number of important chemical processes occur, each cell of the body is in itself a manufacturing plant.

The arteries lead to the capillaries, which are very small, thin-walled vessels penetrating to every part of the body. Some of the liquid portion of the blood passes through these thin walls into the lymph spaces surrounding the cells. Thus the cells are in direct

contact with the lymph, and the lymph with the capillaries, and exchange of materials between blood and cell can occur by diffusion across the very small distance separating them.

All cells take from the blood stream the materials required for their own maintenance and growth. In addition to this, many cells elaborate substances which are used in other parts of the body. This is especially true of the cells of the numerous glands. The secretions of some of these glands are carried by special ducts to the place where they are used, as is the case with the salivary glands, which empty into the mouth by ducts, and the pancreas, which pours its secretion into the intestine through a duct. Many glands secrete substances which do not find their way into special ducts, but which are carried by the blood stream. Some of these secretions have very important effects, either over the whole body or in some part far removed from the gland producing it. Thus the secretion of the pituitary gland has an effect on the general growth of the body, that of the thyroid gland has a stimulating effect on oxidation in the body, and that of the parathyroids a depressing effect on the nervous system. Secretin, formed by some of the cells of the walls of the small intestine, stimulates the secretion of the pancreas. Such substances as have been mentioned are called hormones. Many more of them are produced, and each has a regulatory effect on the development or activity of some part of the body. When all are produced in the right amounts, the parts of the body are well coördinated and normal growth and activity

go on. The distribution of these substances is an important function of the blood.

In the course of the activity of cells, waste products are formed as the result of catabolic processes. The accumulation of these products would poison the cell producing them, but they are given off into the blood stream, and carried through the capillaries into the veins, and are eliminated from the body by the various organs of excretion, the lungs, skin, intestine, and kidneys.

**Metabolism of Carbohydrates: Glycogen.**—On passing through the walls of the intestine, the sugars resulting from the digestion of carbohydrate foods enter the capillaries leading to the portal vein and are carried to the liver. After a meal rich in carbohydrates, the sugar content of the blood of the portal vein may be as high as 0.3 per cent. The usual amount in the blood is about 0.1 per cent. Much of the sugar disappears from the blood of the portal vein when it reaches the liver. This organ is able to convert the simple sugars, glucose, fructose, and galactose, into glycogen, a colloidal polysaccharide whose chemistry has been discussed. After a meal, the liver may contain glycogen to the extent of 12 to 16 per cent of its weight. This compound is gradually rehydrolyzed and supplied to the blood at such a rate that the sugar content of the blood flowing from the liver remains practically constant at about 0.1 per cent. All of the cells of the body use glucose, oxidizing it as a source of energy. Due to their relatively large amount and their activity, the muscles use much more of it than

other organs. The muscles, and other tissues as well, are able to change glucose from the blood into glycogen and store it temporarily. The formation and hydrolysis of glycogen serve to regulate the amount of sugar in the blood. The excess is stored temporarily and, again made available as sugar, is used in various parts of the body.

**Oxidation.**—The principal use made of sugar in the body is its oxidation with the liberation of energy. The oxygen required for this process is carried to the cells from the lungs by the blood. It is held in loose combination by the red conjugated protein, hemoglobin, which forms a part of the red corpuscles. The products of the oxidation are carbon dioxide and water.

Due to this oxidation, the concentration of carbon dioxide is greater in the cells than in the blood. The blood tends to come into equilibrium with this higher concentration by taking up carbon dioxide, a little in combination with the blood proteins, mostly in inorganic combination as bicarbonates, and a little in solution. The carbon dioxide is carried in this way through the veins to the lungs. The concentration of carbon dioxide in the lungs is less than that in the blood of the veins; therefore carbon dioxide leaves the blood and diffuses into the air of the lungs. In this way, this waste product of metabolism is excreted from the body. The water produced may be used in the body as is water from any other source, and the excess is removed through the lungs or skin by evaporation, or through the kidneys. There is no doubt that compounds intermediate between sugar and



carbon dioxide and water are formed during this oxidation, and it is possible that lactic acid is one of these, since it occurs in muscles.

**Anaërobic Respiration.**—In the presence of sufficient sugar, a considerable amount of respiration may occur in the absence of oxygen. In such cases sugar is both the reducing agent and the oxidizing agent. Some of the sugar is oxidized to carbon dioxide and water, and at the same time some of it is reduced to compounds containing less oxygen. Alcoholic fermentation, in which carbon dioxide and ethyl alcohol are formed from sugar, is a case of this kind. Similar changes may occur in the body; the result of one such change is the formation of fat from sugar. Fats contain a much lower per cent of oxygen than the sugars, and so must be formed by their reduction.

**Carbohydrates from Other Sources.**—The liver is able to form glycogen from other compounds than sugars, among which are pyruvic acid and other ketonic acids that result from the deaminization of amino acids. Deaminization occurs due to bacterial action in the intestine, and the liver itself also is able to remove the amine group from some amino acids, provided more are available than are used for protein synthesis in the body. Thus a considerable part of the protein used as food may be converted into carbohydrates. Glycogen also may be formed from the glycerol resulting from the hydrolysis of fats, but the fatty acids are not converted in this way; there is no proof that they ever give rise to carbohydrates in the body.



**Metabolism of Fats.**—The absorption of fats into the lymph has been described. The neutral fats in this fluid do not differ greatly from those in the food. They are in emulsion, and in this condition are emptied into the blood stream through the thoracic duct. Distributed throughout the body by the blood, they are used by the cells in three somewhat different ways. They may be used as the source of fats or other lipoids in the various living tissues. Used in this way, they are changed sufficiently so that the fat of a given tissue is quite characteristic, no matter what the source of the fat in the food. Fat also may be stored as a reserve in the connective tissues of the body, which is especially important, since the storage of carbohydrate is very temporary, but that of fats may be quite permanent. The principal places where fats are stored are under the skin and around the internal organs.

Both tissue and storage fats also are produced from the fats formed by the reduction of sugars in the body. The nature of the storage fat depends to a large extent on the nature of the fats in the food; thus too much oily seeds in the feed of hogs causes them to produce lard that is very soft.

**Oxidation of Fats.**—Fats also are oxidized directly in the body, and it is probable that they are hydrolyzed before they are oxidized. As has been said, glycogen may be formed from glycerol, but it is uncertain whether all the glycerol derived from the fats is converted into carbohydrate before being oxidized, or whether part or all of it is oxidized di-

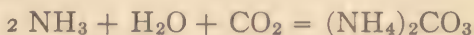
rectly to carbon dioxide and water. The final products of the oxidation of fatty acids are carbon dioxide and water, which are eliminated just as are the final products of the oxidation of carbohydrates. Undoubtedly many intermediate compounds are formed during the oxidation of the fatty acids, and under certain conditions some of these fail to be oxidized further and are excreted through the kidneys. The most important of these are  $\beta$ -hydroxybutyric acid,  $\text{CH}_3\text{CHOHCH}_2\text{COOH}$ , acetoacetic acid,  $\text{CH}_3\text{COCH}_2\text{COOH}$ , and acetone,  $\text{CH}_3\text{COCH}_3$ .

Since fat is a more or less permanent form of storage, it can serve to supply the energy needed during rather long periods of starvation. The excess carbohydrates in the body are used up very quickly.

**Endogenous Protein Metabolism: Synthesis of Body Proteins.**—The amino acids resulting from the digestion of the proteins of the food are absorbed into the blood stream, carried by the portal vein to the liver, and then distributed to all parts of the body by the general circulation. The individual cells remove such of these compounds as are required to build up the proteins of their own protoplasm. Amino acids are never present in the blood in large amounts, as they are removed very rapidly by the cells. If more amino acids are absorbed than the cells can use they are disposed of in a way to be mentioned presently.

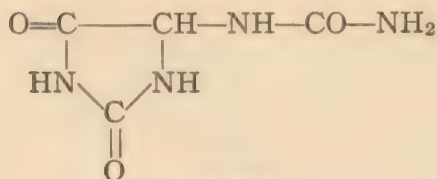
**Waste Products of Body Proteins.**—In the course of the activity of living cells, the protoplasm of which they are composed gradually breaks down; and since proteins are very essential constituents of

the protoplasm, these are destroyed. The destruction of these proteins is an oxidation process, in which much of the carbon and hydrogen of the molecule is oxidized to carbon dioxide and water. The proteins are not completely oxidized in the body, but nitrogen-containing fragments are left which escape oxidation. The principal one of these is ammonia, which forms ammonium carbonate with the carbon dioxide always present, and then is converted, either in the cells themselves or in the liver, to urea, which is the diamide of carbonic acid, and is formed from ammonium carbonate by the loss of two molecules of water:

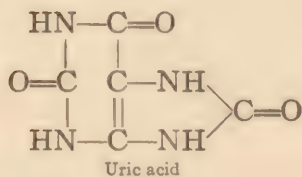


Urea is a waste product which is excreted through the kidneys. Not all the ammonia formed in the body is changed to urea, but some of it is used to neutralize certain acids produced in the body or taken accidentally, and the ammonium salts of these acids are excreted in the urine. The amount of nitrogen excreted in this way is usually small, but may vary widely.

During the breaking down of the proteins of the cell nuclei, the purine bases which form a part of nucleic acid are set free and partially oxidized. In most of the mammals the purine bases are oxidized almost entirely to allantoin, but in man about 98 per cent of them are oxidized only to uric acid, in which form they are excreted.

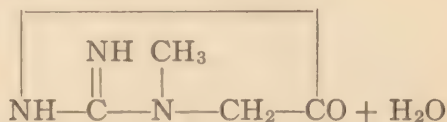
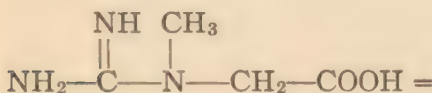


Allantoin



Uric acid

Several other compounds of nitrogen are excreted in relatively small amounts. An important one of these is creatinine, which is undoubtedly formed by the loss of a molecule of water from creatine, which is present in considerable amounts in the tissues of the body.



The origin of the creatine in the body is not known definitely, but it may be formed from the amino acid arginine.

Just how rapid the decomposition of body proteins is, is not known because the body is able to use part

of the decomposition products, along with substances formed by the partial decomposition of the carbohydrates, to resynthesize some of the amino acids. Thus the apparent rate of the destruction of proteins is probably slower than the actual rate.

**Exogenous Protein Metabolism.**—The removal of the amine group from the amino acids has been mentioned. This deamination occurs in the intestine due to bacterial action, in the liver, and perhaps in other organs. The products of the action are ammonia and the ketone acid corresponding to the amino acid. It involves oxidation as well as removal of the  $\text{NH}_2$  group. The ketone acids may be changed to glycogen in the liver, and so be used as sources of energy. The ammonia is converted, largely in the liver, to urea, as was described above, and this compound is excreted through the kidneys.

The proportion of the amino acids derived from the food protein that is deaminized in this way, without having been synthesized into body protein, varies widely, but may amount to at least 60 per cent of the total. The extent of deamination depends largely on the amount of protein in the food. If this is reduced, little deamination occurs and most of the amino acids are used in the reconstruction of the proteins of the cells. On the other hand, if large amounts of protein are consumed, a much larger portion of it is deaminized. As there is no real storage of protein in the body, this reaction serves as a means of disposing of the protein food in excess of the body's immediate needs.

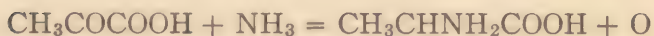


**The Protein Requirement.**—How much protein should be included in the diet is an important question which is hard to answer. The estimate made by Voit, of 120 grams of protein a day for a man of average weight, was based on a study of the amount used by families in moderate circumstances. This is very much more than is really required. Certainly one-half that amount covers the actual need of the body, and 75 grams would meet the daily requirement and provide an excess sufficient to meet any emergencies that might arise.

Since the proteins are the most expensive foods, since their energy is not utilized completely in the body, and since their metabolism involves the extra work of the formation and excretion of urea and uric acid, it would seem that it would be desirable to reduce the amount of protein in the diet to the least amount that will meet the body's needs, plus a reasonable margin of safety. The decreased protein would have to be replaced by increased amounts of fats and carbohydrates, since these act as spacers of proteins in at least two ways. They furnish energy much more easily and economically than the proteins, and when they are present in abundance the oxidation of proteins as sources of energy is decreased. On the other hand, large amounts of protein in the diet not only lead to their oxidation, but also increase the oxidation of carbohydrates and fats. In other words, the proteins are heating foods.

The carbohydrates, by their partial decomposition, furnish fragments (ketone acids) which the body is

able to combine with the ammonia resulting from the decomposition of proteins, to form new amino acids. This reaction is just the reverse of the one already given for deaminization. For pyruvic acid it may be represented as follows:



The amino acid formed in this case is alanine. Thus, in the presence of sufficient carbohydrate, a part of the waste nitrogen may be used over and over again, and the loss of nitrogen is reduced to a minimum.

With proper care in the selection of foods, it is undoubtedly true that a very great reduction in the protein intake may be made safely; in many cases the health has been improved remarkably by this means. There is no doubt that many Americans eat very much more protein than Voit's estimate of 120 grams a day, and often to the detriment of their health.

There are, however, some facts that make doubtful the value of decreasing the protein intake very greatly. It is well known that the most progressive races consume relatively large amounts of protein, but it is uncertain whether this is necessarily true.

**The Amino Acid Requirement.**—From what has been said of the course of digestion, it is evident that the body needs not proteins as such, but the amino acids of which they are composed. From the amino-acids supplied them the cells select those required to construct their own specific proteins. So the important question is not so much how much protein is needed,

as how completely the protein used supplies the required amino acids.

It has been stated that the body is able to construct certain amino acids, but there are some that are required that the body is not able to synthesize. As far as our present knowledge goes, the most important of these are cystine, lysine, tyrosine, tryptophane, and either histidine or arginine; if either of the last two is supplied, the other can be formed from it. Certain proteins lack one or more of these acids, or contain them in insignificant amounts; thus gelatin lacks cystine, tyrosine, and tryptophane; and zein, one of the proteins of corn, lacks lysine and tryptophane. Such a substance used as the sole source of protein would not support growth or maintain life. Although many proteins are complete, it is safer to eat more protein than the minimum requirement, and protein from various sources, in order to be sure of securing an abundant supply of all the amino-acids.

The protein requirement of growing animals is higher than that of mature ones, since new cells are being formed. The same is true of pregnant animals, and the production of milk, eggs, and wool all require large amounts of protein above that necessary to maintain the body alone.

**Energy Metabolism: the Source of Energy.**—In the preceding pages the use of foods as the source of energy has been mentioned frequently. This energy is produced by the oxidation of foods, or of the body substance derived from foods, and it may appear in different forms, such as heat, work, and chemical

energy. Fortunately it is possible to convert these forms of energy into terms of heat, so that the income and outgo of energy may be measured in units of the same kind and their amounts and sources studied. Very careful experiments of this kind have shown that the combustion of materials in the body is the *only* source of its energy. The law of the conservation of energy applies here as well as in the inanimate world.

**Energy Income: the Bomb Calorimeter.**—In such experiments account must be taken of all the exchanges of matter and of energy between the body and its surroundings. The intake of energy is represented by the food eaten, and by any loss of the fats, carbohydrates, or proteins present in the body. The energy content of the foods used is found by determining their heats of combustion. Samples of the food are burned in an apparatus called a bomb calorimeter. The weighed sample is placed in a heavy metal bomb into which oxygen is forced under about 20 atmospheres pressure. In the presence of such a high concentration of oxygen, the food is burned very quickly when it is ignited by means of the burning out, by an electric current, of a very fine iron wire. The bomb is surrounded by a known amount of water at a known temperature; the heat evolved by the oxidation of the sample raises the temperature of the water a little; and the rise in temperature is measured by a very sensitive thermometer. Since the unit of heat, the calorie, is the heat required to raise the temperature of 1 gram of water  $1^{\circ}$ , the heat of combustion



of the sample may be calculated. The number of grams of water surrounding the bomb, multiplied by the number of degrees its temperature is raised, gives the number of calories liberated by the oxidation of the sample. When proper corrections are made for radiation from the apparatus, the heat absorbed by the bomb, etc., very accurate results can be obtained. By means of determinations of this kind, the total amount of energy ingested in the food is found.

**Energy Outgo: the Respiration Calorimeter.—**

The energy outgo includes several items, each of which will be mentioned and discussed briefly. In order that all of these may be measured, it is necessary that the man or other animal serving as the subject of the study should be kept in a small, perfectly insulated room called a respiration calorimeter. This room serves much the same purpose as the bomb in the bomb calorimeter.

Since the animal body is warmer than its surroundings, a large amount of energy is lost by radiation. The heat given off in this way is taken up by water circulating in pipes inside the chamber, and its amount is found in the same way as was given above for the bomb calorimeter.

The evaporation of water from the surface of the body and through the lungs aids in disposing of the surplus heat of the body. The energy required to change the water from the liquid to the gaseous condition becomes latent. The amount of water given off by the body into the air of the respiration chamber can be determined, and since the heat of vaporization



of water is known, it is possible to calculate the amount of energy used in this way.

Work is being done constantly in the body. The beating of the heart, the action of the lungs, maintaining the position of the body, and many other functions, use energy which appears as heat. As long as all this is done inside the respiration chamber, all the heat is retained, and serves either to raise the temperature of the water circulating in the closed pipes, or to evaporate water. In either case its amount is determined by the methods given above. It is evident, then, that the values obtained by these methods include the energy used in performing work.

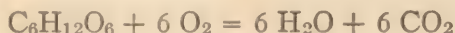
By no means all the food that is eaten is digested, and the undigested residues contain part of the energy determined by the bomb calorimeter. It is necessary to know the amount of energy lost in this way, which is found by determining the dry weight of the feces and their heat of combustion. Certain gases formed by bacterial action in the intestine, such as methane and hydrogen, also contain energy which the body is unable to use, and the amounts of these formed must be determined. Since their heats of combustion are known, the energy lost in this way can be calculated.

Even the proteins that are digested are not oxidized completely. Their nitrogen is excreted through the kidneys in the form of compounds containing carbon and hydrogen, such as urea and uric acid. It is necessary also to determine the amount of energy lost in this way.

The gain of body substance, either fat, carbohydrate,

or protein, causes an apparent loss of energy, and so must be included in the energy outgo. The storage of a gram of fat renders potential 9.54 Calories, that of a gram of protein 5.65 Calories, and that of a gram of carbohydrate (glycogen) 4.19 Calories.

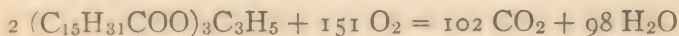
**The Respiratory Quotient.**—In order to complete the data as to the material exchanges, it is necessary to know the amount of oxygen used in respiration and the amount of carbon dioxide given off. This information is needed especially in calculating the kind and amount of body substance gained or lost. The ratio between the volume of carbon dioxide evolved and the volume of oxygen used is called the "respiratory quotient," and is of especial interest as indicating the kind of material being oxidized. According to Avagadro's hypothesis, equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. Thus the respiratory quotient really is a measure of the relation between the number of molecules of carbon dioxide evolved and the number of molecules of oxygen ( $O_2$ ) used. In the complete oxidation of carbohydrates according to the equation



the quotient would be

$$\frac{6 CO_2}{6 O_2} = 1.$$

The oxidation of the fat tripalmitin according to the equation



would give a value for the respiratory quotient of

$$\frac{102 \text{ CO}_2}{151 \text{ O}_2} = 0.67 +$$

The average value for fats is about 0.7, and the average respiratory quotient for the oxidation of proteins in the body is about 0.8, or intermediate between that for fats and that for carbohydrates. The amount of protein oxidized may be estimated from the amount of nitrogen excreted. Using this value, the respiratory quotient, and the total amount of carbon dioxide evolved, it is possible to calculate the amounts of fats, carbohydrates, and proteins burned. The results obtained by such complete and accurate experiments as have been described, form the foundation of the modern science of nutrition.

**The Energy Requirement.**—Obtained partly by this method and partly in somewhat simpler ways, the following table shows the amount of energy required per hour by a man of average size under the conditions stated:

	<i>Calories</i>
Sleeping .....	65
Sitting at rest.....	100
Standing at rest.....	115
Light exercise.....	170
Active exercise.....	290
Severe exercise.....	450
Very severe exercise.....	600

The protein requirement has been discussed in a previous paragraph, but at that time no mention was

made of the effect of work on the amount of protein needed. Because the muscles consist principally of proteins, it has been supposed that protein foods are required to support severe muscular work. This is not the case. There is very little, if any, more destruction of protein during hard work than at rest, provided fats and carbohydrates are supplied in sufficient amount. The extra energy used may be obtained entirely from these substances that are free from nitrogen. Not only is this true, but also energy is obtained much more easily and economically from fats and carbohydrates than from proteins.

Compared on the basis of their energy content, fats and carbohydrates supply the body with energy equally well. Weight for weight, of course, the fats supply more than twice as much energy as the carbohydrates. The diet, then, should contain sufficient protein to meet the protein requirement with a liberal allowance for safety, and the remainder of the energy required should be supplied by fats and carbohydrates.

**Digestibility: Available Energy.**—Experiments with the respiration calorimeter such as have been described require very complicated and expensive apparatus and are very time consuming. Though they give the best information on nutrition, a great deal has been learned by somewhat simpler methods.

The heats of combustion of foods, determined by the bomb calorimeter, give the energy liberated when the food being studied is all completely oxidized. Only that part of the food which is digested and absorbed into the blood stream can be oxidized in the body,



and very few foods are digested completely. Therefore the total energy of the food found by burning it in the bomb calorimeter does not represent its energy value to the body. In order to determine the available energy of a food, or the proportion of the total which actually may be liberated in the body, it is necessary to know the digestibility of the food. This is usually found by feeding the material in question, and determining the amount of it in the feces. The digestibility of the same food differs greatly with different species of animals. Hundreds of determinations of this kind have been made, and the results have been assembled in the standard books on human nutrition, and on the feeding of farm animals. Digestibility is usually expressed in per cent. Further losses of energy are caused by the formation of combustible gases in the intestine by bacterial action, and by the excretion in the urine of compounds not completely oxidized. When all these losses are subtracted from the total energy of a food, the available energy, or metabolizable energy, is left.

**Net Energy.**—Not all the metabolizable energy may be of use to the body for maintenance, growth, or production. This is due to the fact that the ingestion of food results in increased heat production. The exact reasons for the increase are not known. Part of it is due to the work of mastication, a little to the movement of the walls of the stomach and intestines during digestion, and perhaps a small part to the work of secretion of digestive fluids by the glands. The greater part of this energy cannot be accounted



for in these ways, but seems to be due to a stimulating effect of the food itself on oxidation, resulting in the production of excess heat, which is lost by radiation or evaporation and appears to serve no essential function in the body. Whatever the cause, a very considerable portion of the available energy of the food is lost in this way, and its amount varies widely for different foods. The energy remaining after subtracting this from the available energy is called the net energy of the food, and is the real measure of the value of a food as a source of energy. The following table shows the available and net energy values of a few feeds in per cent of their total energy:

Feed	Available Energy, Per Cent	Net Energy, Per Cent
Timothy hay.....	41.00	23.75
Alfalfa hay.....	44.00	17.20
Oats straw.....	35.80	12.95
Corn meal.....	74.90	42.60
Wheat bran.....	55.40	29.45

These determinations were made with steers, and for other animals the values might be quite different. It might be supposed that the net energy values of a feed would differ with its use, whether maintenance, growth, fattening, work, or the production of milk. As far as the information available at present goes, the net energy values of foods are nearly the same for all these purposes except for milk production. In

this case, the net energy values are higher than for the other uses mentioned.

**Minerals.**—Some of the functions of the mineral elements have been discussed. Normal maintenance or growth are impossible unless an adequate supply of these essential elements is provided. This is especially important during the growth of young animals, when new tissue and bone are being formed. If the diet is sufficiently varied, there is little danger of mineral deficiency, especially if green foods are used freely, as they usually contain the important mineral elements in relatively large amounts.

**Vitamins.**—The requirements for life and growth discussed so far are water, oxygen, fats, carbohydrates, proteins containing the necessary amino-acids in sufficient amount, and the essential mineral elements. It is found, however, that even when all these are supplied, normal life and development are impossible except in the presence of certain accessory substances of unknown chemical nature. At one time it was thought that one of these had been isolated, and that it was a complex amine. Although that point is very uncertain, it suggested the name "vitamin" which has been used for all of these substances. At present, three of these vitamins having somewhat different properties and functions have been recognized.

The antineuritic, or water soluble, vitamin is present in the seed coats of grains, in yeast, in milk, and some other animal products, as well as in fresh vegetables. Its absence from the diet causes a disease of the nerves called beri-beri, which is prevalent in

certain regions where a restricted diet consisting principally of polished rice is used.

The fat soluble, or growth promoting, vitamin is especially abundant in green leaves and in butter fat. Growth appears to be impossible without this substance, and the resistance of the body to the invasion of bacteria seems to be increased by its presence.

The antiscorbutic vitamin occurs abundantly in fresh vegetables, in certain fruit juices, in fresh meat, and in milk. Scurvy has been especially abundant on shipboard on long voyages when provisions of the kinds mentioned have been exhausted. Although all the vitamins are more or less sensitive to heat, the antiscorbutic vitamin is especially so. An infant fed for some time on sterilized or pasteurized milk is likely to develop scurvy unless the vitamin is supplied by the use of some such material as orange juice or tomato juice.

Apparently animal bodies are unable to form the vitamins. Although certain animal products, such as milk and meat, contain some of these substances, it is probable that they were formed by plants, and only stored in the animal body.

It is quite likely that there are other substances like the three vitamins described. The whole subject of these accessory food substances is one of the most interesting problems of nutrition, and is being studied intensively in many laboratories.



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